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Microwave Processing Of Fiber Reinforced Composites (Optimization of Glass Reinforced Epoxy Curing Process)

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MICROWAVE PROCESSING OF FIBER REFINFORCED COMPOSITES

(Optimization of Glass Reinforced Epoxy Curing Process)

By

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To Amr Khaled…

The mastermind of "LIFE MAKERS"

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Abstract

Microwave curing of polymer matrix composites has proven to be an attractive substitute for conventional thermal curing. Industrial applications are currently developed including telecommunications, aerospace, food industry, enhancement concrete setting, composites manufacturing, and many others. Many universities and research centers around the globe are endeavoring to make use of this technology to the most. Common research objectives include homogeneity of the cure, the acceleration of cure kinetics, cure reaction mechanism, and enhancement of mechanical properties. In order to efficiently utilize this form of energy, precise control over power, temperature, and time were applied to achieve set goals: reduce cure time and thermal overshoots, assure complete cure, and maximize mechanical properties. This work discusses an optimization scenario to achieve these set goals by combining data from calorimetric analysis, insitu temperature and power monitoring, and energy conservation studies. An experimental setup is assembled consisting of laboratory equipped multi mode microwave applicator and programmable feedback controllers. For thermal curing, a typical electric furnace is used with three thermocouples measuring the cavity, mold, and sample temperatures. Test samples consisted of both neat blend of DGEBA resin together with samples of glass fiber reinforced epoxy. Prior to testing, the microwave cavity has been calibrated to approximate heat losses in the system and thus determine the expected data accuracy. Curing experiments for a specific temperature-time profile show that microwave applicator not only follows the set temperature but also eliminates thermal lag and temperature overshoot. While holdback technique could not deliver the required cure cycle, PID control strategy succeeded in homogenously curing successful epoxy and epoxy/fiberglass samples. Kinetic knowledge is enriched using DSC to determine expected curing times at different curing temperatures. Based on these data, a selected isothermal temperature of 100 °C was used with variable dwell times between 13-30 minutes for microwave curing. Mechanical testing data shows that microwave cured samples have

relatively exceeded the conventionally cured ones in both flexural strength and modulus. The DSC recommended time of cure 13 minutes, at 100 °C, is a good approximate which suggests similar curing mechanism of cure kinetics in both thermal and microwave methods. High ramp rate, 200 °C/min could also be achieved without material degradation or temperature overshoot by carefully controlling power during the ramp stage. Effect of gelation time and vacuum degassing, being a major time saving area, were also tested. The gelation time has particularly enhanced the flexural modulus of the epoxy samples. In short, the use of efficient process controller resulted in superior mechanical properties at practically optimum time durations.

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Chapter 1

INTRODUCTION

Chapter 1

Introduction

1.1 Statement of the problem & Field of Study

Microwave curing has immerged as a feasible replacement of conventional thermal curing technique. In this project, we are comparing between both techniques to highlight the processing and performance advantages of microwave heat delivery. In addition, we are researching in the optimization of microwave power delivery for curing of epoxy matrix composites. The approach of this problem is to control all process parameters, power, temperature, and curing time, in order to obtain the maximum mechanical properties. The hoped outcome is to achieve a high quality composite with maximum mechanical properties and minimum cycle time and enrich our knowledge about the thermal, kinetic, and electromagnetic behavior during microwave heat delivery.

1.2 Need of the study

Achieving an optimized curing cycle was the goal of many researchers. Some of them have used experimental trial and error approaches and some have used advanced numerical models. The common approach was to achieve the highest mechanical properties in lowest energy levels. Definitely energy here is directly related to time, temperature, and other processing conditions.

The conventional oven heating has, in fact, complicated these optimization efforts due to many reasons as will be explained later. On the other hand, microwave heating has been suggested as a better alternative.

Microwave heating of materials is relatively a new technology immerged at the start of this century. Although there are nowadays many industrial applications in this field, we can not say that researchers have reached the optimum design of this process. There are still also many debated issues. For example, how microwave energy interact with polymers functional groups is still a riddle. Another example is mechanical properties. Many researchers claim the increase in mechanical properties while others believe that mechanical properties of both conventional and microwave curing are comparable. The obvious reason for this conflict is the different type of MW generators, non unified experimental setups & measurement techniques, different matrix/fiber combinations, and mostly limited control systems over the process. We will analyze the various claims of current researches in the literature review section. In conclusion, we are still experiencing need for enriching our knowledge in this vital source of energy and explore the possible effects on physical, chemical, and mechanical properties of polymer matrix composites.

In short, we want to examine to effect of microwave heating on mechanical properties, homogeneity of curing, and completeness of polymerization process. The second objective is to 'tune' this process through the use of advanced, programmable controllers to assure that the actual cure cycle matches the planned one. In addition, building an electromagnetic and curing kinetic model will certainly facilitate potential optimization algorithm. The results of our analysis will be in form of Mechanical testing results, real time curing charts, process parameters such as power consumed, temperature, and time, all supported by kinetic modeling of the process.

1.3 Thesis Tasks

The assigned research work consisted of both technical and academic tasks. These include:

1. Searching the global market to find the best "quality vs. cost" microwave setup to assure efficient heating of the material. The search contained also the different concept of microwave heating, microwave hardware, different power and temperature measurement tools. In other words, a microwave processing laboratory had to be constructed to satisfy both the current and future research plans in this field. Beside the microwave system, forming molds, holders, and other experimental accessories had to be designed and manufactured.
2. Carrying out a literature review to identify all the current research objectives on microwave processing of polymers and polymer based composites. The Literature reviewed contained journal papers, books, encyclopedias, master and PhD thesis, and internet websites.
3. Full thermal characterization of the epoxy resin used using Differential scanning calorimetry. An experimental model is also built to simulate the kinetic behavior of the resin.
4. Calibration of the power absorption of the microwave applicator using water and resin samples. Heating losses and efficiency are calculated and compared to manufacturer standard.
5. Oven curing of resin and composite samples according to a standard isothermal cure cycle.
6. Preparing an experimental program to cure both epoxy and glass fiber composites using the microwave applicator and record the power consumed, temperature variation, and cure time. Based on each set of samples the program was modified to achieve the optimum heating scenario and assure defect free and complete control over the cycle.
7. Mechanical testing of flexural strength and modulus using three-point bend test.
8. Analysis of the experimental data and issuance of process recommendations and future research plans.

1.4 Thesis Organization

This thesis is subdivided into six chapters. Each contains a unique content of the research activities:

- Chapter one includes brief description of the problem to be solved and the set of objectives to be achieved. Furthermore, detailed thesis tasks are explained showing both the technical and academic research activities.
- Chapter two is devoted to microwave fundamentals. These include explanation of the microwave generation and propagation mechanisms, classification of materials according to microwave interaction and dielectric properties, comparative advantages over thermal energy, and the various types of microwave generation devices.
- Chapter three contains a comprehensive literature review on the historical development of microwave energy applications starting from communications and military purposes and ending with industrial and domestic applications. The industrial applications are then generally introduced with partial concentration on material processing of ceramics, a major research interest in this field. Finally, all the major research work in the last two decades in microwave processing of polymers and polymer composites are discussed in details.
- Chapter four includes complete description of the material used in the testing. The experimental setup is also explained accompanied with figures and design drawings. In addition the analytical and testing equipment like DSC and three-point bending machine are also discussed with reference to the international standard applied.
- Chapter five demonstrates the findings of the experimental work including thermal and microwave curing, DSC analysis, efficiency testing, and mechanical testing. This chapter also contains data analysis in light of the current findings and literature comparison. Also it includes expected sources for inaccuracy and recommendations for future development.

Chapter 2

MICROWAVE PROCESSING FUNDEMENTALS

Chapter 2

Microwave Processing Fundamentals

2.1 Microwave propagation Theory

Microwaves are considered to be a portion of the electromagnetic spectrum with wavelengths from 1 mm to 1 m with corresponding frequencies between 300 MHz and 300 GHz. (Thostenson & Chou, 1999A). Two particular frequencies are chosen by the Federal Communications Commission (FCC) for industrial, scientific, and medical (ISM) purposes. These two most commonly used frequencies are 0.915 and 2.45 GHz. An electromagnetic wave is a sinusoidal wave consisting of both an electric and magnetic components as Maxwell stated in 1873. The right hand rule applies to the orientation of this wave as the index finger indicates the direction of propagation, the extended thumb indicates the alignment of the electric field, and the palm indicates the alignment of the magnetic field [Figure 2.1]. The electromagnetic wave in principle is accelerated charged particles, such as electrons, produced usually with numerous electric circuits as we will see later on the section of processing systems.

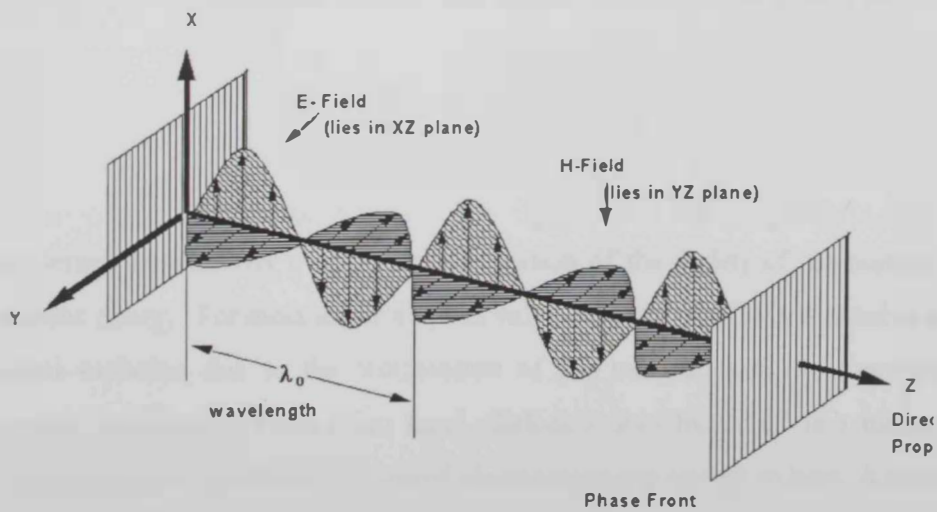

Figure 2.1: Schematic of Electromagnetic Wave (Webpage 1)

2.2 Microwave/Material Interaction

The main group of properties responsible for material behavior under microwave fields is its dielectric properties. Dielectric properties are usually presented by two parameters, dielectric constant ε' or the permittivity and dielectric loss factor ε''. They can be both represented in this complex dielectric constant ε^* (National Materials Board, 1994):

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \qquad (2.1)$$

The two terms can be presented by non dimensional terms relative to the permittivity of free space:

$$\varepsilon_r' = \frac{\varepsilon'}{\varepsilon_0} \qquad (2.2)$$

$$\varepsilon_r'' = \frac{\varepsilon''}{\varepsilon_0} \qquad (2.3)$$

Where the permittivity of free space, ε_0 is equal to $8.854X10^{-12}$ F/m.

Another simple representation of the relative permittivity is related to the relative capacitance of the material. If a DC voltage is applied to a two parallel plate capacitor with vacuum separation, a capacitance value of C_o will develop presenting the amount of charge stored in vacuum. By inserting a material, however, the capacitance will increase to the value of C indicating higher amount of charge storage. The relative permittivity will then become:

$$\varepsilon_r' = \frac{C}{C_0} \qquad (2.4)$$

In physical terms, Permittivity ε' is a characterization of the ability of the material to store electromagnetic energy. For most materials, this value can realistically be treated as a constant with minimal variation due to the temperature of the material and the frequency of the electromagnetic radiation. On the other hand, dielectric loss factor ε'' is a measure of the ability of the material to transform the stored electromagnetic energy to heat. A material with

a high dielectric loss does not store the energy effectively, and a significant portion of the energy is converted ("lost") to thermal energy within the material (McConnell, 1999).

A low-loss material, with a low value of ε'', is able to store electromagnetic energy well and does not absorb much of the stored energy. In these cases, the material may be said to have a permittivity, ε', which is essentially just the real part of the complex permittivity because the imaginary part is so small as to be negligible. A lossy material, with a high value of ε'', absorbs a larger portion of the electromagnetic energy instead of storing it all. The absorbed energy is converted into thermal energy within the material through several dissipation mechanisms. Lossy materials are often characterized by a quantity known as the loss tangent, tan δ:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \qquad (2.5)$$

In addition the power dissipated inside the lossy material in a finite sized element can be mathematically represented as follows:

$$dP = 2\pi f \varepsilon_0 \varepsilon'' |E|^2 dV \qquad (2.6)$$

Where dP is the finite dissipated power in Watts, f is the source frequency which equals 2.45 GHz for common industrial microwaves, |E| is the RMS magnitude of the electric field (V/m), and dV is the volume of the finite element (m^3).

Using the previous equations we can classify materials into three categories based on interaction with the microwave field (David et al., 2000). First category is transparent material through which microwave pass with minimal absorption. These materials have very low dielectric loss factor (ε''). Examples include Teflon, which has a dielectric loss of about 0.0003. That is why Teflon is a common material to be used in manufacturing microwave molds. The second category, commonly known as 'opaque' materials, includes all electric conductors. These materials reflect microwave energy with minimal absorption of the microwaves. Conductive materials usually have free electrons which are not tightly bound to any particular atom structure, unlike dielectrics. These free electrons will migrate through the material in the presence of an applied electric field, losing energy by resistive dissipation due

to collisions with other electrons and atoms in the lattice structure. Figure 2.2 demonstrates the repulsive force generated at the surface of a conductor preventing the microwaves from penetrating through the material.

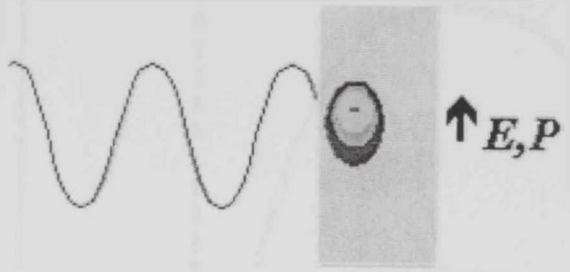

Figure 2.2: Microwaves reflectance in conductors (Webpage 2)

The last category is absorbing material or dielectric material. These materials have relatively high dielectric loss factor which means that the waves are attenuated inside the material and "lost" as heat (David, 2000). Figure 2.3 shows the relationship between the amount of power absorbed and the dielectric loss factor. The three categories of materials are demonstrated. We can notice that by increasing the loss factor more heat is lost inside the material and thus more power absorbed. However, after certain value the amount of heat lost becomes very high. The electromagnetic wave will not even penetrate through the surface as all the energy is dissipated at the surface. The material is said to reflect the wave. The three categories of material are schematically demonstrated in Figure 2.4. We can notice that thermoset could have properties of both transparent and receptive or absorber materials. Another remark is that water has the highest power absorption rate. As we will see later, this phenomenon can be explained in light of the dipoles freedom of water molecules.

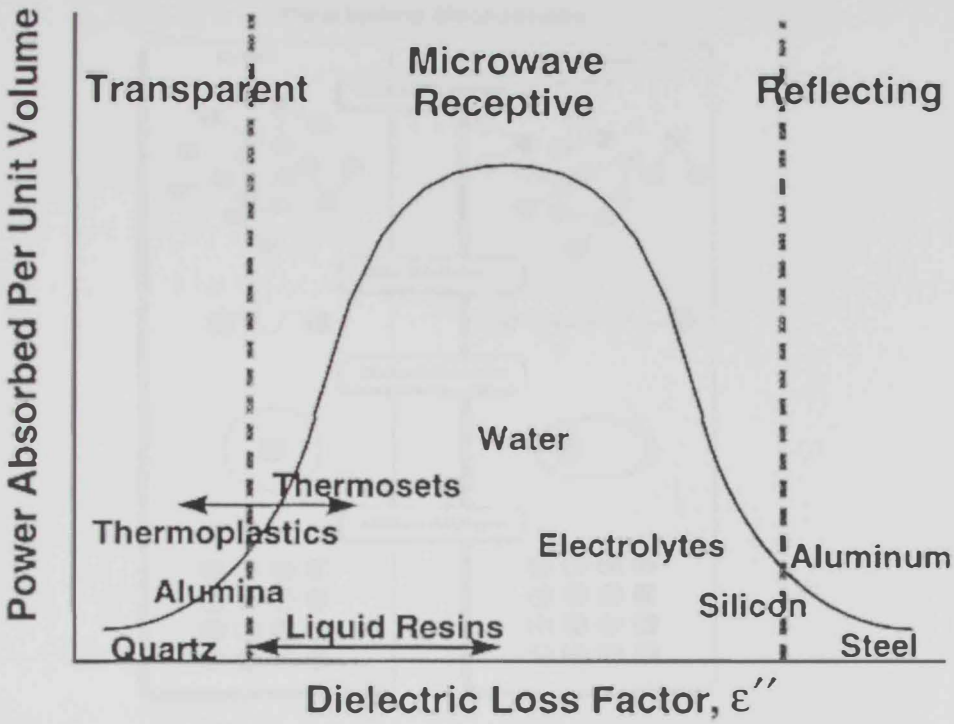

Figure 2.3: Power Absorption of Microwave energy Vs dielectric loss factor (Thostenson & Chou, 1999A)

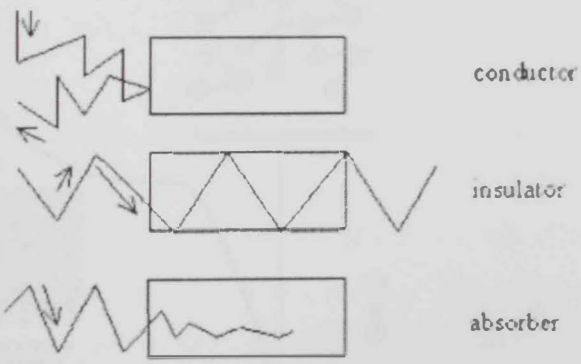

Figure 2.4: Schematic representation of Microwave Materials (Jones et al., 2002)

MW Energy dissipation mechanisms can be subdivided into 4 main categories: space charge polarization, ionic polarization, electronic polarization, and dipole alignment [Figure 2.5] (Theury, 1992). A specific range of frequency covers each dissipation mechanism [Figure 2.6]. From this figure, the most essential mechanism at microwave frequency of 2.45 GHz is dipole alignment or orientation polarization.

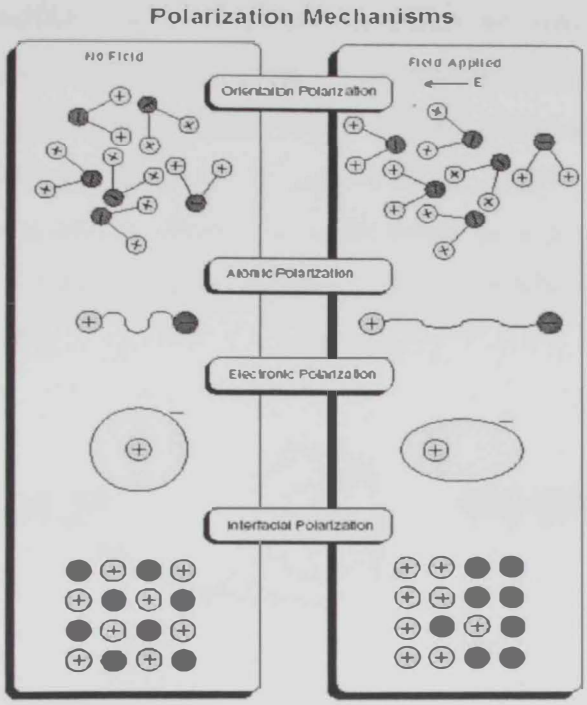

Figure 2.5: Schematic presentation of polarization mechanisms

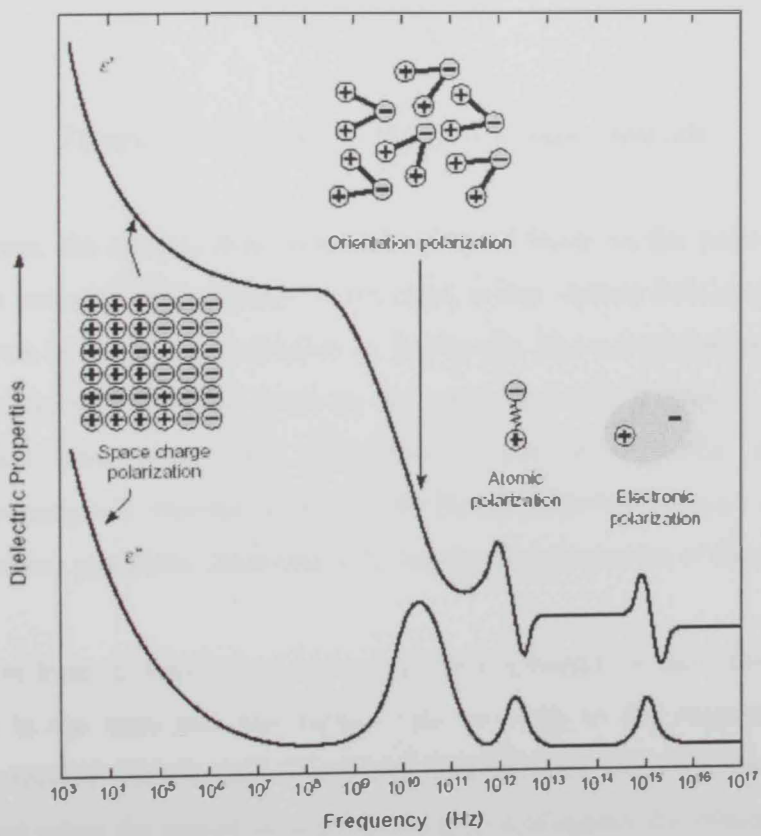

Figure 2.6: Variation of Polarization mechanism with frequency

In general, molecular dipoles are generated by non-uniform distribution of electrons in the molecule. The most significant case is water molecules H_2O, an extremely high MW absorber [Figure 2.7]. In water molecule, the two hydrogen atoms and the one oxygen are not arranged in a line. The H-O-H angle is 104.9° rather than 180°. This nonlinear configuration together with the different electronegativity of H and O atoms creates an asymmetric charge distribution within the molecule, which can be described by a permanent electric dipole. Therefore, the oxygen will have a partial negative charge $O^{\delta-}$, while the hydrogen will have a partial positive charge $H^{\delta+}$.

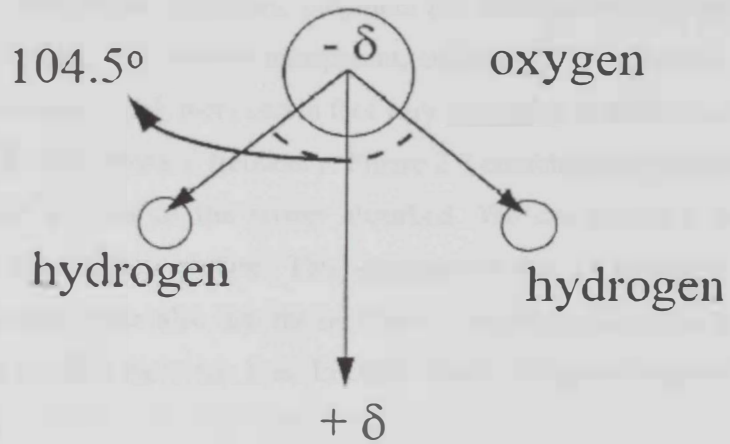

Figure 2.7: Schematic of the H-O-H water molecule

In this mechanism, the electric field exerts a rotational force on the polar moment of the molecules in the material. The polarity, or direction, of the electric field component reverses at every half-cycle of the radiation frequency and results in a corresponding reversal in the direction of the exerted rotational force on the molecules. The resistance to rotation will instantly generate heat, which will volumetrically heat the material. In other words, microwave processing will virtually eliminate the Residual thermal stresses originating from the large temperature gradients, diminishing the mechanical properties of the processed part.

Another common term in microwave interaction with materials is the relaxation time. The relaxation time is the time that the dipoles take to settle in the original position upon neutralizing the applied electric field. Therefore, the maximum rate of microwave heating in solids is achieved when the period of applied electric field equals the relaxation time of the polarization. We can conclude from the previous explanation that by monitoring the dielectric

properties of the material, significant process parameters can be controlled and more control can be imposed over the heating process. Furthermore, microwave energy can be an economic source of energy if compared to the long time consumed and the elevated temperatures required in sintering of ceramics, for example.

2.2.1 Behavior of Polymers & Polymer Composites

In order for us to understand and realize the applications of microwave energy in polymer processing, later in chapter 3, we should first concentrate more on how polymers interact with microwave fields. Similar to all materials, polymers fall into the two categories out of the three mentioned previously: Microwave transparent, and microwave absorber as was shown in figure 2.3. The behavior of polymers can in fact vary according to their structure, operating temperature, and applied microwave frequency. Figure 2.8 combines the effect of temperature and frequency on the amount of the power absorbed. We can notice a decrease in the dielectric loss after certain temperature. This decrease is due to relaxation phenomenon explained above. We can notice also that the increase in frequency increases the temperature required to achieve a specific dielectric loss. In other words, at higher frequency material has lower dielectric loss.

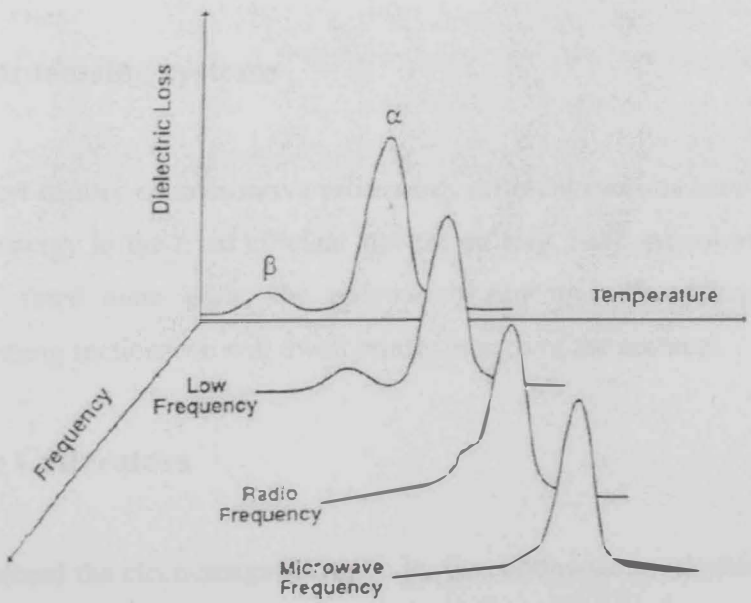

Figure 2.8: Effect of Temperature and frequency on dielectric loss factor (National Materials Board, 1994)

The effect of polymer structure, on the other hand, can be directly related to the dipole moment. Microwave coupling to a given dipole will be greater in a liquid, less in a rubber, and even further reduced in a glassy or crystalline polymer. Polymers dielectric constant can vary during a processing cycle or if a phase change occurs, solvent is removed, frequency is modified. These external effects change the type and concentration of dipoles. The principal mechanism of microwave absorption is the reorientation of dipoles in the imposed electric field. The materials with the greatest dipole mobility will exhibit the most efficient coupling. Microwave heating, therefore, will couple most efficiently with the strongest dipole in a system and has the potential to selectively heat polar polymers in mixtures. This advantage, if used carefully, will lead to unique microstructures and thus unique qualities. As an example, multi-phase materials can be heated so that the highest loss factor phase will heat higher and therefore the final microstructure will be dissimilar to the one produced by thermal heating. For the case of two phase composites of low conductivity fibers, such as glass fibers, the dielectric properties of the composite are dominated by the dielectric loss of the resin rather than the fiber. In other words, studying the resin properties and the cure profile can be directly related to the cure behavior of glass reinforced composite (Thostenson & Chou, 1999A). On the other hand, carbon fibers, being conductive, dominate the dielectric properties of the composite. For this reason it will be shown later in chapter 5 that we focused more on the resin itself in our study of fiber glass composites.

2.3 Microwave processing systems

Through out the short history of microwave processing, different systems have been used to deliver microwave energy in the most efficient and secure way. Each microwave processing system consists of three main parts, the microwave generator, transmission line, and applicator. In the coming sections we will dwell briefly in each of the sections.

2.3.1 Microwave Generators

We have already defined the electromagnetic wave by the continuous acceleration of charges in a certain frequency. A generator is the device used to accelerate these charges. Much development work took place in microwave generators to cope with the spreading applications of microwave energy. The historical efforts in this field, beginning at 1920, are

outlined in Figure 2.9. From this figure we can determine that modern processing systems rely on a variety of ways to accelerate and decelerate electrons. Common types of microwave generators include magnetrons, klystrons, traveling wave tubes (TWTs), and gyrotrons.

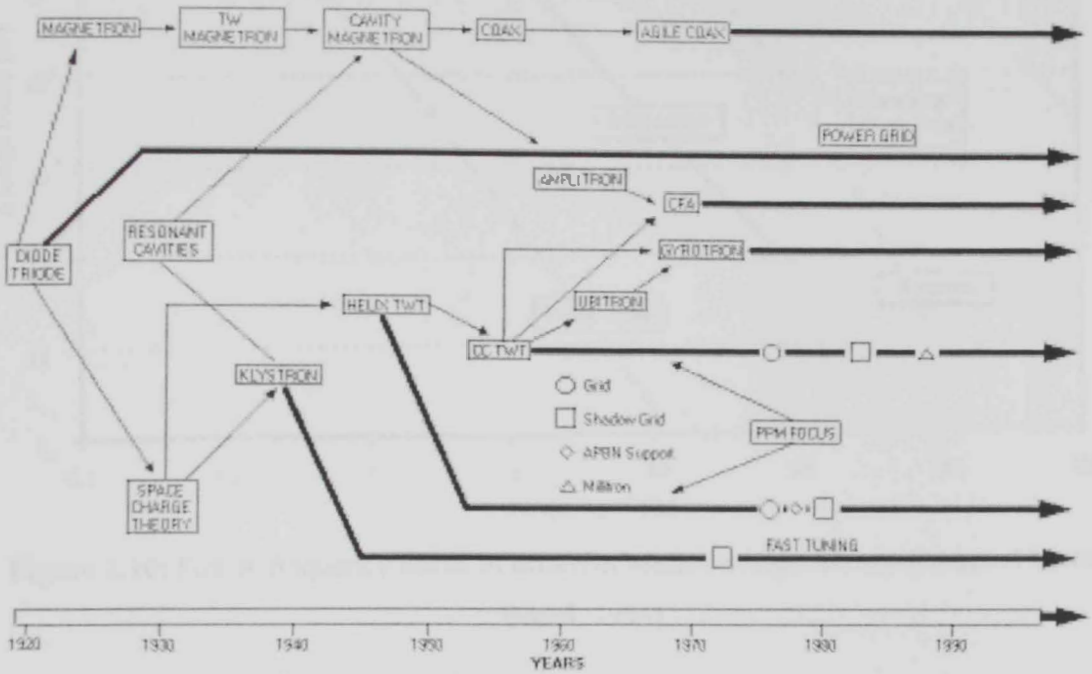

Figure 2.9: Development of Microwave Generators (National Materials Board, 1994)

Each device is constructed to operate in a specific power and frequency range as shown in Figure 2.10 Covering each of these types is beyond the scope of this work. We will concentrate more on magnetrons, being the most efficient, reliable, less expensive, and wide-spreading.

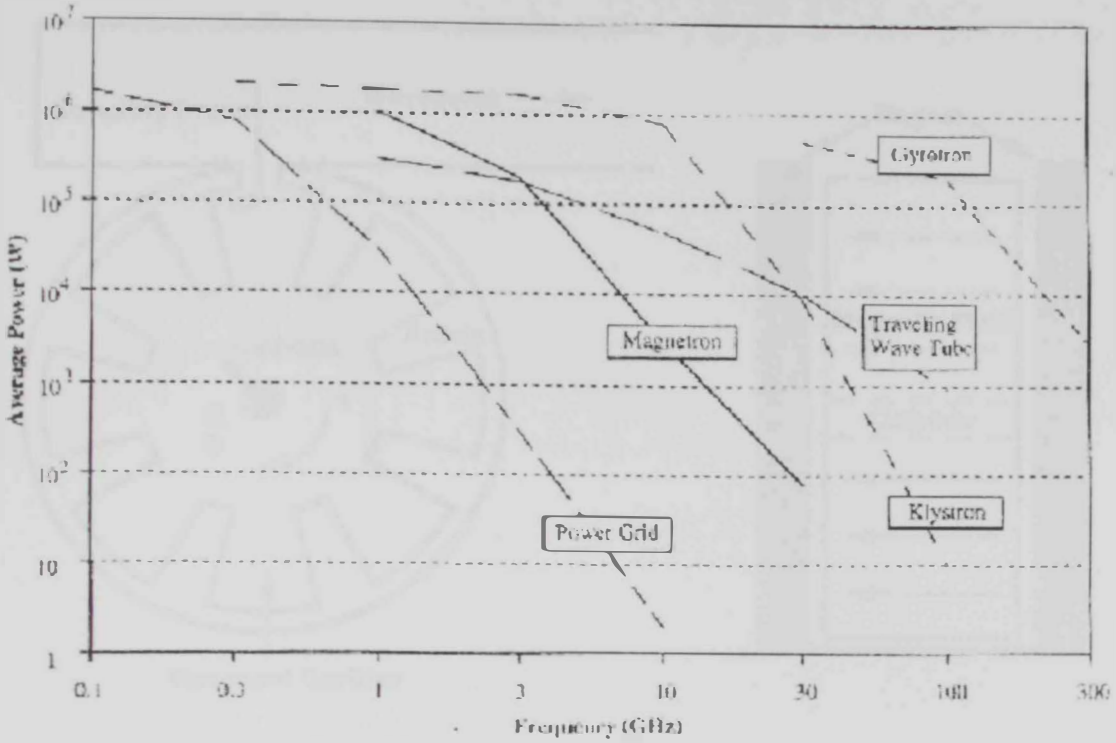

Figure 2.10: Power-frequency limits of different Microwave generators (National Materials Board, 1994)

Magnetron was the first device to use the interrelation between the acceleration of electrons and a time-varying electromagnetic field to produce microwave energy. Early magnetron units generated pulses of electromagnetic energy output but later units were capable of continuous output. Typical home ovens have an output of about 700-800 W with efficiencies approaching 65%. On the other hand, industrial magnetrons produce power ratings of several thousands of watts with higher efficiency and reliability. Figure 2.11 shows a schematic diagram of magnetron. From this figure, an external magnet is used to create a magnetic field orthogonal to the electric field, and the applied magnetic field creates a circumferential force on the electron as it is accelerated to the anode. The force causes the electron to travel in a spiral direction, and this creates a swirling cloud of electrons. As electrons pass the resonant cavities, the cavities set up oscillations in the electron cloud, and the frequency of the oscillations depends on the size of the cavities. Electromagnetic energy is then coupled from one of the resonant cavities to the transmission lines (Thostenson & Chou, 1999A).

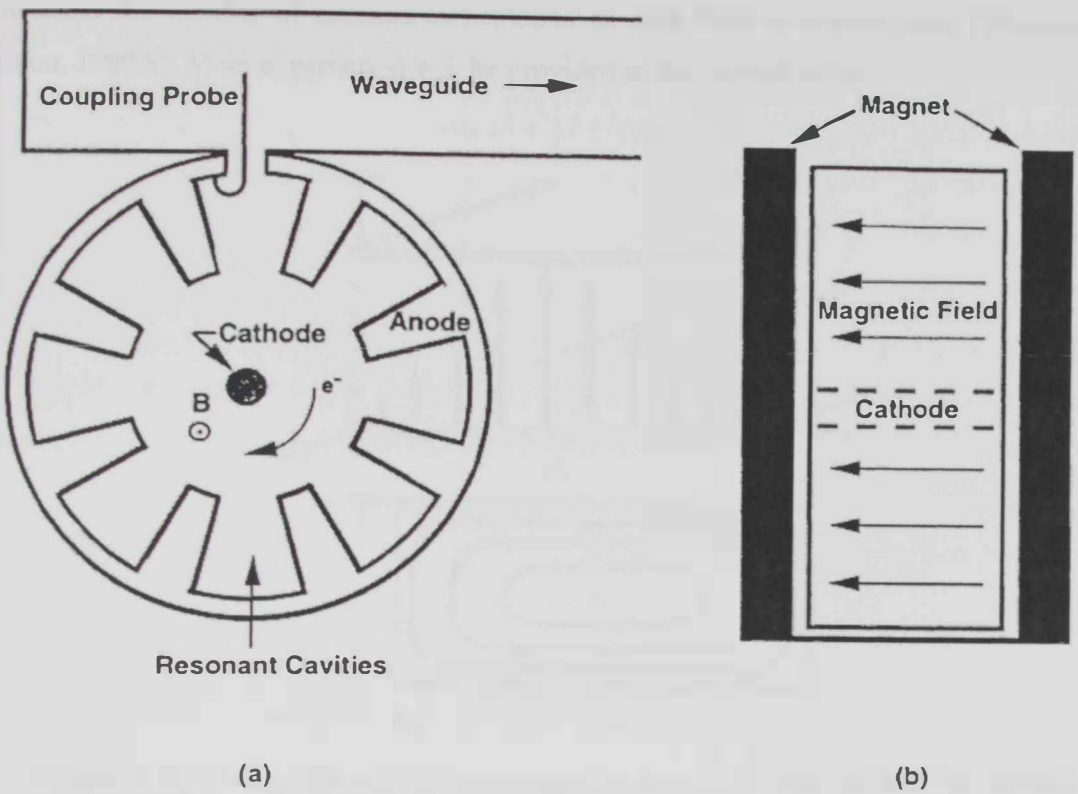

Figure 2.11: Schematic diagram of Magnetron: (a) Top View, (b) side view (Thostenson & Chou, 1999A)

2.3.2 Transmission Lines

Transmission lines have the function of transferring the generated electromagnetic waves to the applicator where it is used for processing. A specific type of transmission line is selected according to the power rating, the service frequency, and the distance between the generator and the applicator. For low power systems, coaxial cables is used, similar to the one used on linking the antenna to the TV set. However, at higher frequencies and power output, waveguides are used. They consist of hollow tubes of constant cross section used because of their low attenuation and high power handling capability. Microwaves propagate in waveguides in two possible modes: transverse electric TE and transverse magnetic TM. For the TE mode, the electric field in the direction of propagation is zero. For the TM mode the magnetic intensity in the propagation direction is zero. Every mathematical solution of the electromagnetic wave in a rectangular waveguide can be decomposed into a linear combination of the TE and TM modes. The most common waveguide mode is the TE_{10} mode as shown in Figure 2.12. The subscripts specify the mode of propagation, and the mode

indicates the number of maxima and minima of each field in a waveguide (Thostenson & Chou, 1999A). More explanation will be provided in the coming section.

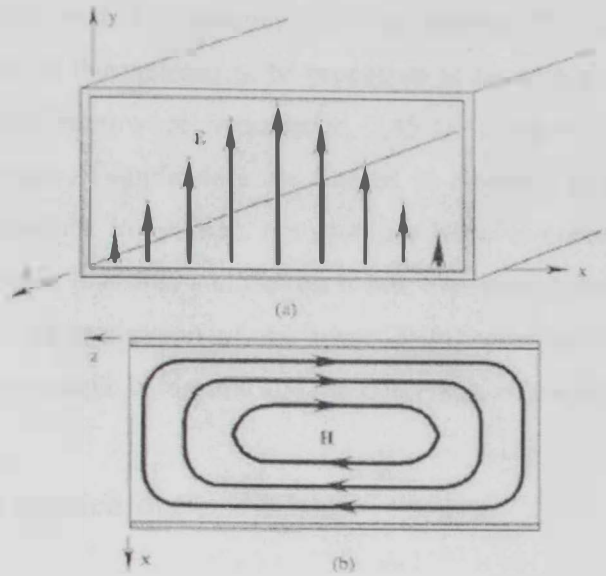

Figure 2.12: Waveguide with TE_{10} propagation mode: (a) cross section, (b) elevation. (Roussy and Pierce, 1995)

2.3.3 Microwave applicators:

Microwave applicators are devices designed to heat a material in the most efficient, reliable, repeatable, and economic way. The design of these applicators highly depends on the type and the size of the material to be heated. Single mode and multi mode applicators are the most common types. Each of these types has its own advantages and disadvantages that will control any selection process for any industrial or research application.

In general, a "mode" is a propagating electromagnetic wave of a given frequency. A microwave source may generate a single frequency, but the output wave may reflect inside and interact with the applicator before the wave reaches the material to be heated. This results in microwave energy of different orientations being present inside the applicator. Each orientation of waves present in the applicator is called a "mode".

2.3.3.1 Single mode applicators:

A single mode applicator is an applicator of a single electromagnetic wave orientation. A propagating single wave with one maxima and one minima fills in the cavity. This will definitely limit the size of the material to be processed to be within one wave length of the microwave. At common microwave frequencies, 2.45 GHz, the wavelength is very small. Consequently, these types of applicators are limited to research purposes only rather than industrial large-sized product. In addition, hot spots are likely to occur in large sized samples where some of the material is heated and the rest is not. The main advantage of this type is the possibility of accurate determination of the wave distribution inside the cavity and thus careful placement of the sample is feasible and the efficiency of heating is thus much higher.

2.3.3.2 Multimode applicators:

From the name, multimode applicators are capable of sustaining a number of high order modes at the same time. This type of applicator is used in home microwave ovens. By increasing the size of the microwave cavity, the number of possible resonant modes also increases. Consequently, multi-mode applicators are usually much larger than one wavelength. For a rectangular cavity, the mode equation for the resonant frequencies is (Thostenson & Chou, 1999A):

$$f_{nml} = c\left[\left(\frac{l}{2d}\right)^2 + \left(\frac{m}{2b}\right)^2 + \left(\frac{n}{2a}\right)^2\right]^{1/2} \qquad (2.7)$$

where f_{nml} is the resonant frequency above which a specific mode is possible; c is the speed of light; n, m, l, are the number of half-sinusoid variations in the standing wave pattern along the x, y, and z-axes; a, b, and d are the dimensions of the cavity in the x, y, and z directions.

Compared to the features of previously explained single mode, multimode applicators have solved many of single mode disadvantages. For example, the presence of different modes results in multiple hot spots within the microwave cavity. By exciting as much orientations or modes in the cavity and carefully mixing them together, the time average power distribution will become more uniform and much suitable for large sized samples. From the above

equation it is clear that by increasing the size of the cavity more modes are suitable as the resonant frequency required to generate these modes deteriorates. In the experimental setup section, we will mention all other techniques used to assure maximum uniformity of heating.

2.4 Benefits of Microwave Energy

What make microwave energy attractive are the significant advantages over conventional thermal heating. In conventional heating, the heat source causes the molecules to react from the surface toward the center so that successive layers of molecules heat in turn. This operation will take a long time and will always generate a lag between the oven temperature and the temperature in the sample. In other words, the temperature control is more difficult and hot spots are likely to occur due to non-uniform distribution of temperature. Rather on depending on heat diffusion from the surface of the sample, the electromagnetic waves of the microwave energy penetrate the surface of the material and directly interact with the material. In case of steep thermal gradients, process induced residual stress are likely to occur (Thostenson & Chou, 1997). The expected result of microwave processing is volumetric heating or reversed thermal gradients. Due to this penetrating nature of the microwave energy, time of processing is extensively reduced. Reversed thermal gradients, on the other hand leads to desirable results, especially in thick polymer composites sections where inside-out heating is a major requirement. Not only does microwave energy reverse the thermal gradient inside the material, but it in fact reduces the amount of this gradient due to the volumetric heating nature. The impact of this benefit is the reduction in internal stresses which could lead to cracking in severe heating rates. We will dwell in this topic in details in literature review.

Another advantage of microwave energy is selective heating of materials. The electromagnetic wave will couple with some materials with certain dielectric properties. In multiple phase materials, such as ceramics, the microwave will couple with the higher loss phase. Unique microstructures could be achieved by efficiently utilizing this feature. In addition, microwave transparent materials can be heated by embedding phases in the form of fibers, granules, or layers to enhance heating process.

Economically speaking, microwave systems have been found as efficient energy replacement for their conventional counterparts. This conclusion was drawn after a comprehensive study

by National Materials Advisory Board NMAB in the mid nineties (1994). The main finding of this study is the fact that the cost of capital equipment for microwave processing differs widely and depends on power rating, frequency, size, applicator design, manufacturers, and market volume of the equipment. The higher initial cost of the investment seems for the first glimpse as a drawback of microwave energy. This thought is even further strengthened by the fact that microwave heating may only result in 30% of the energy transfer compared to conventional heating methods from a given quantity of fossil fuel (National Materials Board, 1994). This is due to losses in converting fossil fuels into electricity, converting the electricity to microwave energy, and the conversion of microwave energy into heat within the material. However, the speed of the process, the volumetric heating, better product quality, the compaction of the equipment size, in most cases tip the scales for the microwave energy. For example, the energy savings in drying and firing of ceramics using microwave energy is as much as 80% of its conventional rival while in alumina sintering can be as high as 90%. (Sheppard, 1988). Table 2.1 summarizes other cost savings for some ceramics and polymer adhesives. In conclusion, the potential of microwave energy is higher than the conventional counterpart due to the continuous improvement in process design, equipment size, and final product quality.

Table 2.1: Productivity improvement and time savings of some ceramics and polymers (Ku et al., 2002)

Materials	Process	Timesavings	Productivity improvement
Whiteware	Slip casting	66%	Immediate mould recycling
Whiteware	Drying	24 h to 8 min	
Whiteware	Overall process	70%	6.25 pieces to 27 pieces per worker per day
Boron carbide	Sintering	> 90%	
Structural adhesive	Curing	66%	66% cost reduction
Varnish	Curing	< 70%	

2.5 Challenges in Microwave Energy

From the above discussion, Microwave energy appears to be a promising process of heating. However, we should not expect placing a sample of resin in an electromagnetic field and expect to cure smoothly without complications. The properties of the electromagnetic field, the chemical composition of the material, structural & thermodynamic changes during processing, size and shape of the material, the distribution of the electromagnetic field, and the physics of the microwave/materials interactions all complicate microwave processing. Microwave devices must be carefully designed to optimize the curing process by eliminating the drawbacks of microwave heating, namely thermal runaway, Hot spots & thermal gradients, and penetration depth.

One of the most critical drawbacks of microwave heating that curb the microwave skyrocketing development is thermal runaway. Let us take the curing process of thermoset-based composites as an example. Initially, microwaves couple well with the resin dipoles. However, as temperature increases, the dielectric loss factor ε'' will increase causing rapid heating, after a critical temperature. In addition to exothermic nature of the cross linking reactions, the risk of temperature overshoot will boost and thus thermal degradation is more likely to occur. When gelation temperature is reached, the viscosity increases, and the dielectric properties begin to deteriorate due to the hindrance of dipole rotation (Thostenson & Chou, 1999) [Figure 2.13]. In other words, dielectric loss factor of thermoset generally increases with temperature and decrease with extent of cure (Jow et al., 1989). Therefore, temperature should be carefully monitored during heating so that any rapid abrupt change in temperature will be automatically interpreted to change in power of the microwave cavity.

Another important aspect in the phenomenon of thermal runaway is the fact that microwave heating depends not only on the rate of the microwave power absorption but also on the ability of the sample to dissipate the heat. In other words, thermal runaway occurs when the material absorbs more energy than it can remove. Thus, the heat input must be greater than the heat conducted away. To avoid thermal runaway, the microwave energy must be altered or the material must be removed from the heated zone. Removing the material from the heated zone is usually not an option, so an applicator that can adjust the electromagnetic field must

be utilized. Knowledge of the dielectric properties of the material to be heated is crucial in the proper design of microwave applicators (Curtis, 1999).

This phenomenon is especially notable in case of using thermally insulated mold. For example, in most of the microwave experiment the polymer sample is molded in Teflon mold which is known to be good thermal insulator and thus the phenomenon is applicable. Therefore, we will try to measure the efficiency of heating by quantifying the amount of losses during heating.

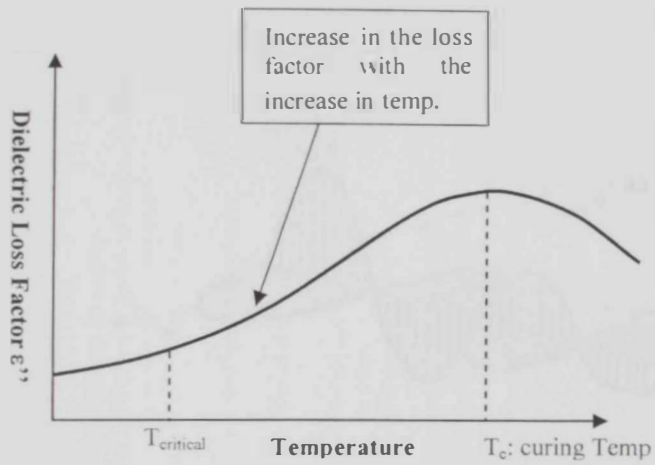

Figure 2.13: Schematic presentation of the expected variations of dielectric loss with temperature

The second drawback is hot spots. The region where the electric field is maximum heats up the material intensely while the zero electric field regions still not heated. The hot spots location will change according to the type of mode of operation, and the number of modes present in the field, single mode or multi modes. We have dealt with this phenomenon in the processing system section and found out that multi mode applicators could provide an answer of solution. More discussion will be provided when describing the experimental setup.

The last microwave drawback is penetration depth. As the material absorbs energy, the strength of the electromagnetic field deteriorates until a certain depth beyond which the electromagnetic field cannot penetrate [Figure 2.14]. Penetration depth is defined as the distance from the surface of the part to the depth where microwave power is 1/e of the absorbed power at the surface. If the penetration depth of the microwave is much less than the

thickness of the material only the surface is heated while the rest of the sample is heated through conduction. The depth of penetration depends on many parameters: frequency and dielectric loss factor as shown in this equation (Thostenson & Chou, 1999):

$$d_p = \frac{c\,\varepsilon^o}{2\pi f \varepsilon''} \qquad (2.8)$$

Where d_p, ε^o, ε'', f are penetration depth, dielectric constant of free space 8.85 x 10^{-12} (F/m), dielectric loss factor, and frequency.

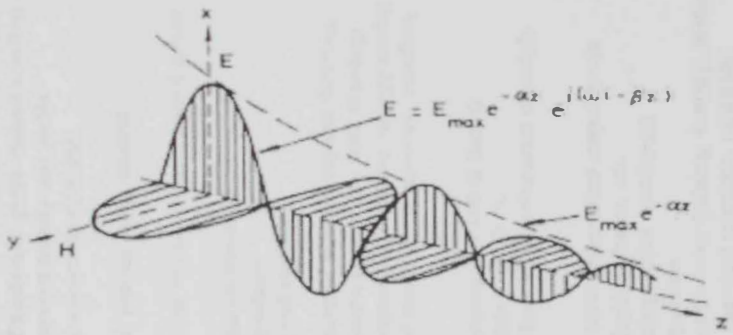

Figure 2.14: Deterioration of the electromagnetic wave in a dielectric material (Metaxis and Meredith, 1983)

Besides the benefits and the challenges explained several other characteristics exist of microwave processing. Table 2.2 summarizes all characteristics of microwave energy including both the advantages over conventional curing and the challenging disadvantages.

Table 2.2: Characteristics of Microwave Energy (National Materials Board, 1994)

Characteristic	Feature	Benefits (over conventional heating)	Disadvantages
1. Penetrating radiation, direct bulk heating	• Materials heat internally • Reversed thermal gradients (ΔT) • Lower surface temperatures	• Potential to heat large sections uniformly • ΔT favors chemical vapor infiltration; matrix infiltration • Reduced skin effect on drying • Removal of binders & gases without cracking • Improved product quality and yields • Materials & composite synthesis	• M/W transparent materials difficult to heat • Hot spots, cracking • Large ΔT in low thermal conductivity materials, and nonuniform heating
	• Instantaneous power/temperature response • Low thermal mass	• Automation, precise temp. control • Rapid response to power level; pulsed power	• Controlling internal temperature • Arcing, plasmas
	• Applicator can be remote from power source	• Heat in clean environment • Materials synthesis • See differential coupling	• Require new equipment designs special reaction vessels
2. Field distributions can be controlled	• High energy concentration • Optimize power level versus time • mm-waves can be focused or defocused, rastered as desired	• Precise heating of selected regions (brazing, welding, plasma generation, fiber drawing) • Process automation, flexibility, energy saving • Synthesis of materials, composites, powders, coatings	• Equipment more costly and complex • Requires specialized equipment
3. Dielectric losses accelerate rapidly above T_{crit}	• Very rapid heating	• Rapid processing (2 - 1000x factor) • Heat materials >2000 °C • Capable to heat M/W transparent materials $>T_{crit}$	• Hot spots, arcing • Nonuniform temperature • Control of thermal runaway
4. Differential coupling of materials	• Selective heating of internal or surface phases, additives or constituents	• Heating of M/W transparent materials via additives, fugitive phases, etc. • Hybrid heating (active containers) • Materials synthesis • Selective zone heating (joining, brazing, sealing) • Controlled chemical reactions, oxidation, reduction; use of M/W transparent containers • Drying, curing, annealing; matrix infiltration	• Reactions with unwanted impurities • Contamination with insulation or other phases
5. Self-limiting	• Selective heating ceases (self-regulating) after certain processes have been completed	• Below critical temperature, drying & curing are self-regulating • Completion of certain phase changes is self-regulating	• Undesired decoupling during heating in certain products • Difficult to maintain temp.

Chapter 3

LITERATURE REVIEW

Chapter 3

Literature Survey

After explaining the main advantages of microwave energy and the mechanism of interaction with materials, we shall review the major research fields related to microwave processing of materials. Scrutinizing literature, we will potentially recognize many conclusions. First, the applications of microwave energy have passed through many stages starting from military applications and ending with personal and industrial ones. Second, Researchers in this field not only have attempted to fully characterize materials behavior due to microwave fields, measurement of mechanical properties for example, but also they have tried to use this sort of energy in unique applications which in some cases became only possible under microwave heating. In addition, they tried to overcome processing difficulties and optimize the final product properties. From this survey we can afterwards introduce our optimization work as another building brick to enrich research knowledge in this field.

The first section covers the historical development of microwave energy, including foremost pioneering research work and microwave applicators. This would give us a clear view on the relative novelty but with skyrocketing pace of development. The second section includes current applications of this energy on microwave processing of materials. We will begin by briefly describing the applications on rubber, wood, and ceramics industry. Afterwards, we shall focus with more details on our main topic, polymers and polymer matrix composites.

3.1 Historical view on Microwave Development

Microwaves have always existed since the dawn of mankind 10 billion years ago. James Maxwell is though considered to be the founder of modern electromagnetic devices. His pioneering Treatise on Electricity and Magnetism in the year 1873 provided a solid scientific background for the propagation of electromagnetic energy (Thuery, 1992). In this work,

Maxwell hypothesized that electric and magnetic fields could propagate through a vacuum at the speed of light via coupled wave components aligned perpendicular to one another as seen in Figure 2.1 in chapter 2. This theory was later verified through the experimental works of Hermann Von Helmholtz and Heinrich Hertz, during the years from 1879 to 1887. Hertz was also the first scientist to intentionally generate electromagnetic waves in the form of radio signals in the lower portion of the microwave frequency band (430 MHz) using a simple electric oscillator. Hertz continued in his experimentation with such devices and was able to confirm the speed of propagation postulated by Maxwell and demonstrated such electromagnetic phenomena as refraction, deflection, polarization, and standing waves due to constructive wave interference (McConnell, 1999).

Ten years later, the scientific community began to join in pioneering this new technology and in the year 1894, Marconi utilized microwave signals at 1.2 GHz to transmit wireless communications over a distance of 4 km. He went on to extend the range of this feat to over-the-horizon communication by the year 1931. At the time of the first microwave communications, the term 'microwave' had yet to be assigned. Clavier, who later went on to demonstrate wireless telephone communication over a distance of 51 km at 1.7 GHz, was the first scientist to use such a phrase.

The next major development in the use of radio frequencies besides communications was the development of systems to detect large metallic objects. The principle was first developed in 1904 by a scientist named Hulsmeyer when he observed that reflected radio signals from large metallic objects could be detected at a great distance. The first military application of his studies were not realized until 1934 when a large emitter/antenna array was mounted aboard a naval vessel for the purpose of detecting other ships under conditions where visual detection would not be possible. A scaled-up version of the device was mounted on a fixed structure for detecting aircraft. These early detectors utilized the same principles of modern radar, but they operated at frequencies below the microwave band due to the power/frequency limitations of the time. However, these early developments paved the way for true microwave band detectors engineered simultaneously in the US and Britain during WWII for installation onboard aircraft. The information from ground-based radar stations no longer had to be radioed to pilots, thus their presence was no longer compromised if detected by the enemy.

When the WWII was about to end, scientists began to recognize other applications of microwaves rather than communication and detection. Since microwave generators in the past had utilized modulated beams produced by pulsing sources for generating microwave signals, the doorway to dedicated microwave heating was opened in the year 1944 by Brown and Derby (Theury, 1992). These scientists created the first Magnetron generator capable of producing a continuous output wave instead of a pulsed one. It was not until 1951 that the first American patent for a microwave oven for food heating was issued. The first American restaurant to serve pre-packaged meals heated by microwaves opened in 1962 using a British microwave generator, which at the time were more economical than similar American units. Microwave heating continued to have far greater prevalence in the commercial food preparation industry than in other industrial applications for quite some time. In the 70's & 80's home ovens became more and more popular until the market for these units peaked in 1984 when it is estimated that 40% of all households in industrialized nations owned a microwave oven.

3.2 Survey on Microwave Processing of Materials

3.2.1 General Applications of microwave Energy

Microwave energy has been the subject of extensive studies during the last few decades as an alternative for the conventional thermal energy. It offers advances to a wide range of industries, including telecommunications, aerospace, scientific instruments, environmental monitoring, biotechnology, food industry, medical applications, material drying, mineral ores extraction, casting molds de-waxing, soil defrosting, asphalt road repair, enhancement concrete setting, electromagnetic drilling, polymers curing, and composites manufacturing. Definitely, covering all of these areas should require more comprehensive researches. Therefore, we shall select some of these applications with more details in the following paragraphs.

In mineral processing, for example, the use of microwave energy has lead to reduction in energy consumption and environmental pollution. By applying the thermal expansion and selective coupling principles, where the electromagnetic waves interact with a precise element

in the mineral compound, electromagnetic waves separate the valuable minerals from the waste material in the mineral ore (Ku et al., 2002).

In the field of food services and agriculture industry, microwave energy has also found considerable amount of attention. Since most food contain reasonable amount of water, microwaves is a very efficient heating medium as it couples very well with the polar water molecules as seen in chapter 2. Enzymatic inactivation, possible by microwave interaction with material, can lead to delayed spoiling in certain fruit and vegetable (Theury, 1992).

In agriculture field, microwave energy not only can be used to prevent frost of crops in cold weather, but it also can be used to terminate unwanted seeds and pests in the soil (Theury, 1992).

A recently developed wood drying application uses the unique microwave characteristic of internal heating (David et al., 2000) [Figure 3.1]. The penetrating nature of microwave energy is used to rapidly and uniformly cure thick, cross-sectional, polymer/wood composite beams as they are pultruded continuously through a die. Instead of using huge lumber beams, which is not environmental friendly, microwave energy will cure wood fibers waste coated with polymeric adhesive in desired structural sections. Strength, consistency and workability make it also an attractive alternative to structural steel. The maximum thickness of wood beams was increased from 2 inches in thermal method to about 12 inch thick in microwave heating (Thostenson & Chou, 1999).

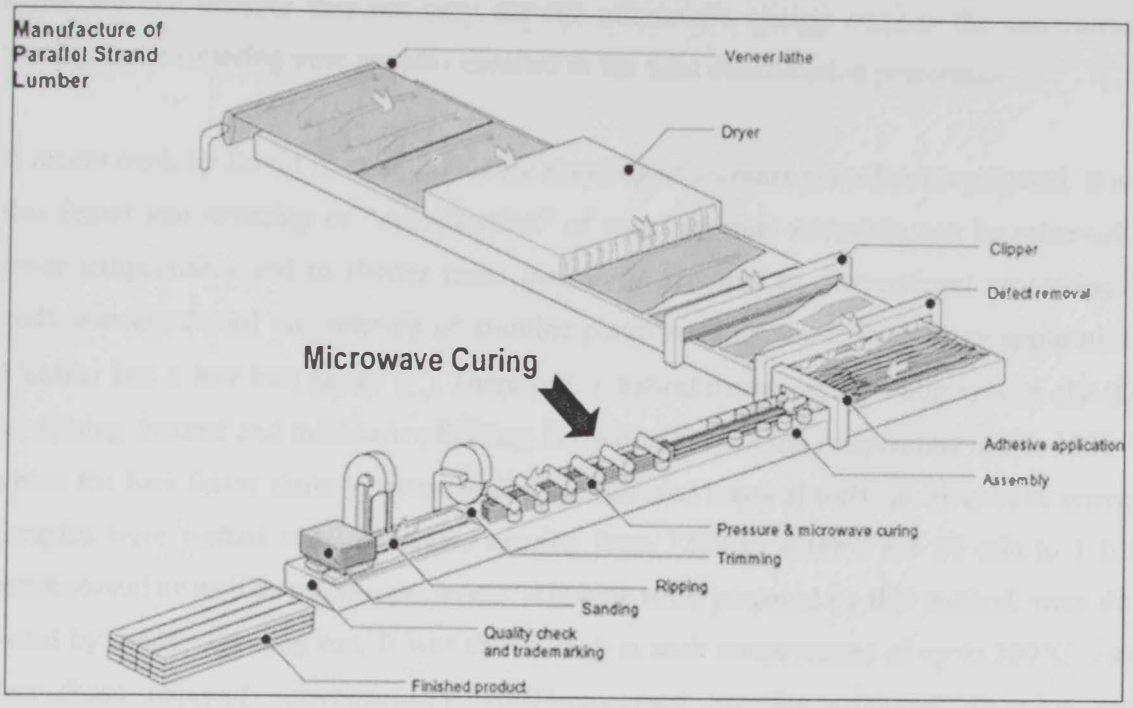

Figure 3.1: Microwave aided manufacturing of Parallel Strand Lumber (Webpage 3)

3.2.2 Processing of Ceramics & Ceramic Matrix Composites

The enthusiasm in materials processing first began in processing of ceramics, namely ceramics sintering. Ceramics sintering process involves applying pressure and heat to a mold filled with granular or powdered material to cause the grains to fuse together into a solid part. Due to extremely low thermal conductivities of most ceramics and at the same time the high dielectric properties, microwave energy has been a successful substitute. For this particular process, microwave heating applicator has resulted in superior product properties with minimum porosity. Due to the fact that the research in this field is very dense and versatile, the next few paragraphs has the mere objective of giving a glimpse about microwave processing of ceramics. The information in these paragraphs can be observed as an introduction for our area of concentration, microwave processing of polymer and polymer matrix composites.

Researchers in this field have reported major decrease in processing times. The process time is the time needed for densification of ceramics granules to take place. Figure 3.2 demonstrates the work conducted on alumina sintering by Janney & Kimrey (1991). From this

figure we can observe that not only did the microwave energy surpass the conventional heating in the sintering time but also excelled in the final densification percentage.

In recent work by David E. et al (2000) the sintering of alumina is further investigated. It was also found that sintering or "densification" of some ceramic materials can be achieved at lower temperatures and in shorter times than those required in conventional processing. A study was conducted on sintering of alumina plates used as armor in military applications. Alumina has a low loss factor ε''. Therefore, a hybrid microwave heating system (HMH), combining thermal and microwave heating, is used to elevate the temperature above 1000 °C where the loss factor starts to increase and the material starts absorbing microwave energy. Samples were soaked at temperatures ranging from 1200 to 1500°C for 30 min to 1 h in conventional as well as microwave ovens. Alumina rods, prepared by this method, were then tested by 4-point bending test. It was shown that, at soak temperatures of up to 300°C lower than those required conventionally, HMH-processed samples produced materials with physical and mechanical properties equal to or superior to those produced conventionally.

The reasons for this phenomenon are explained in light of the microwave characteristics. One possible explanation for these differences may be the internal heating phenomenon associated with microwave processing. When the inside of the sample is allowed to achieve high density before the surface layers densify, the internal porosity is minimized since fewer pores are 'trapped' inside the samples (De & Ahmed, 1991). This remark leads us to believe that the higher the sample size the higher the strength as less porosity is entrapped inside the material. The sample density and cross-sectional uniformity in the density did increase when the sample size was increased from 6 to 20 g. More explanations for this phenomenon will be dealt with when tackling the issues of what is so called "microwave effects", later in this chapter.

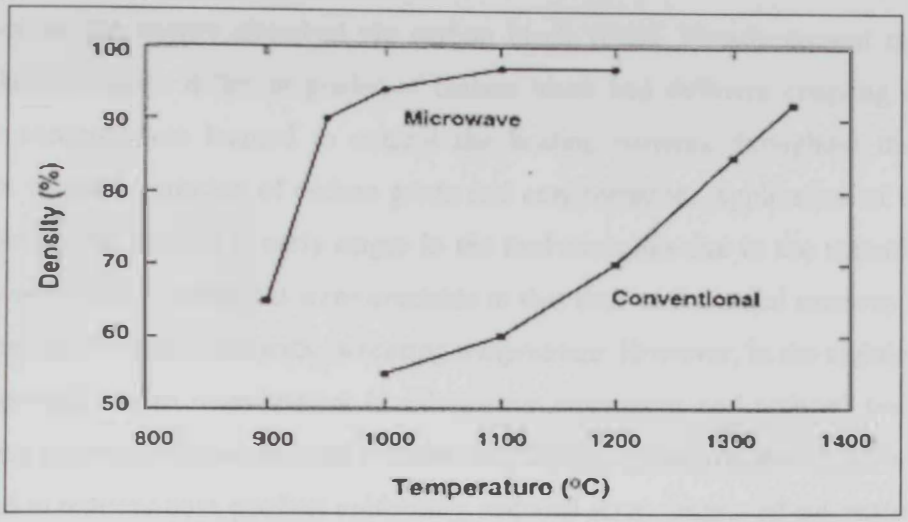

Figure 3.2: Density percentage of MW & Conventional heating sources versus process temperature for Alumina (Janney & Kimerey, 1991)

3.2.3 Processing of Polymers & Polymer Matrix Composites

A wide range of applications is established in polymers processing such as microwave joining of polymers, microwave curing and joining of reinforced polymer matrix composites, pultrusion, and rapid curing of adhesive. In the coming few paragraphs we will try to highlight some of these applications focusing on their industrial outcome and optimization efforts. Some research objectives focus mainly on the applicability of the process while others focus more on the behavior of the material during cure. Common objectives include homogeneity of the cure, enhancement of mechanical properties, and the acceleration of cure kinetics. The collected papers are classified as accurate as possible to illustrate the historical growth of the research field and at the same time to fall into 4 main research objectives: Industrial applications, processing homogeneity, mechanical properties, and microwave effects.

3.2.3.1 Industrial Applications

The earliest successful microwave application in polymers processing is vulcanization of rubber. Vulcanization is a process in which the long monomer chains in the material become cross-linked, which results in parts that retain their shape and elastic properties to a much higher degree than do untreated parts. The principal mechanism of coupling of the microwave

radiation is the energy absorbed via carbon black fillers, already present in many rubber formulations. Since different grades of carbon black had different coupling characteristics, rubber compounders learned to control the heating patterns throughout the multilayered product through variation of carbon grade and concentration. Application of this processing technology was limited at early stages in the mid seventies due to the nonuniformity of the microwave curing ovens that were available at that time and thermal runaway attributable to increases in dielectric loss with increasing temperature. However, in the eighties, the industry was boosted due to development in microwave equipment and reduced cost of operation resulting in over 600 installations worldwide (National Materials Board, 1994). The process resulted in reduced cost, product uniformity, reduced scrap, improved automation and process control (Ku et al., 2002).

Microwave curing techniques have also been applied in microelectronics industry. Silicon chips are attached to Printing Circuit Board (PCB) using polymeric material. Microwave energy is applied in this process to selectively heat the underfills without heating up the PCB and to reduce the cure cycle (Zhou & Hawley, 2003).

Regarding the fiber reinforced industry, high-performance polymeric composites, reinforced with carbon, glass, or aramid fibers, have been effectively used by the aerospace and electronics industries in applications requiring light weight, high specific strength and stiffness, corrosion and chemical resistance, and tailorable thermal-expansion coefficients. The dielectric properties of resin matrix & fibers have made it possible for developing microwave based technologies in printed circuit boards, aviation, and marine fields. However, the hindrance behind the spread and scale up of these applications was mainly the high cost and time of fiber orientation and curing. This is shown in the rapid need for automated forming techniques to assure compaction and defect free products. Microwave, processing, however, have provided feasible solutions for several forming processes.

Another practical application of this technology is based on the work by Lind et al (1991). Thermoplastic polymer, PEEK, reinforced with carbon fiber was successfully prepared using single-mode applicator. PEEK is a high performance, semicrystalline thermoplastic polymer which is usually difficult to heat as being semi transparent to microwave fields at room temperatures. When a critical temperature is reached molecular mobility is increased and permanent dipoles start to form which makes it microwave heatable (Thostenson & Chou,

1999). Enough power was absorbed to rapidly heat the PEEK matrix to melt temperatures so that it could be bonded to a consolidated laminate.

Using the outcome of Lind et al. works, a microwave applicator was designed and preliminary concepts were developed for an automated tape placement process for fabrication of composite parts [Figure 3.3]. This system has particular importance in carbon fiber composites as the penetration depth is small due to carbon high reflectivity. As noticed in the figure the part being formed has curved surface. Therefore, a system has been designed to sense this curvature and adjust the cavity resonance to relocate the hot spot of microwave energy for maximum efficiency.

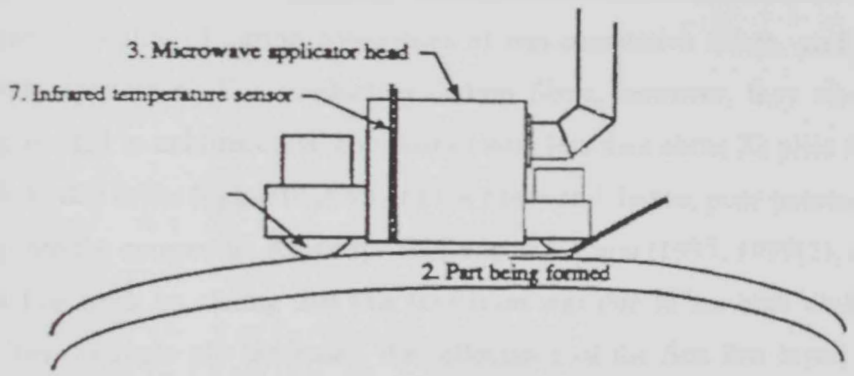

Figure 3.3: Microwave applicator for tape-placement part forming device (Lind et al., 1991)

Furthermore, microwave energy has been found to be a feasible, economic source for composites manufacturing during pultrusion process. Polymeric composite preform is pulled through a heated die, where the shape is molded and the matrix cured. The advantage of using microwave energy lies in the feature of direct energy transfer. Instead of using a processing chamber consisting of a quite long heated die due to the slow heat transfer to the polymer matrix and relatively long cure times, a single-mode resonance cavity has been used to rapidly heat the part using microwave radiation in a significantly shorter process chamber, resulting in less force required to pull the fiber bundle through the die (Methven et al., 1992; Lin & Hawley, 1993; Methven et al., 2000; Qiu et al., 2000). The control process is relatively easier than other forming processes due to the mass production nature of the process and the fixed part configuration in each batch.

3.2.3.2 Homogeneity of Cure

One of the significant challenges in composites is the processing of thick cross-section parts, one inch or more. The conventional processing, oven based, would require complex cure schedule with very slow thermal ramp rates and isothermal holds to control overheating due to cure reaction exotherm and poor thermal conductivity (National Materials Board, 1994). This drawback of oven processing drew the attention of many researchers. Most of the references agree that the earliest attempt for applying microwave technology for thick sections was the work of Lee and Springer (National Materials Board, 1994; Lee & Springer, 1984; Springer, 1992). Not only did they carry out the first curing experiments, but they also developed fundamental electromagnetic models for microwave-material interaction. They also proved the feasibility of curing composites of non-conductive fillers, such as fiberglass, in wave-guide applicators. For conducting carbon fibers, however, they claimed that curing would be limited to unidirectional composites with less than about 32 plies (approximately 7-8 mm thick) due to the high reflectivity of the fibers and, hence, poor penetration depth of the radiation into the composite. Recently, Thostenson & Chou (1997, 1999(1), and 2001) further analyzed Lee work by stating that this limitation was due to the high dielectric loss of the carbon fiber. In angle ply laminates, the reflectance of the first few layers was too high to achieve efficient heating of thick laminates. In addition, the incorporation of high conductivity fibers may result in the formation of local hot spots and electrical arcing. Recently, such problem has been eliminated, using a single-mode microwave cavity.

Followed the work of Lee & Springer, Asmussen et al (1987) used a tunable, single-mode resonant cavity applicator with feedback controller to allow the resonant frequency to be changed as material properties vary during processing. The modification is carried out by varying the size of the microwave cavity and thus changing the electromagnetic distribution inside. Although many other systems were utilized, such as multi-mode cavities, and variable frequency microwave generator VFM, most of the work carried out afterwards was based on such system. Several other works, including the work by Jow et al. (1989), successfully cured epoxy systems at elevated temperatures avoiding thermal degradation.

Boey et al. (1992) also emphasizes the importance of void reduction in the quality of microwave cures epoxy/fiber glass composites. The use of vacuum bagging as an industrial solution is demonstrated and compared to the conventional curing method. By combining the microwave advantage of short cycle time and efficient vacuum bagging technique better-quality composites were obtained.

Using a single-mode system, Wei et al. (1993) successfully cured 36- and 72- ply composites. Heating was controlled through feedback on/off switching of microwave power based on sample temperature as measured using a fluro-optic probe.

Thostenson & Chou (1997) resumed the microwave research using a multi mode microwave cavity with mode stirrers. These mode stirrers are similar to metal fans that rotate inside the cavity reflecting and distributing microwaves. In addition to the large size of the cavity, the mode stirrers helped in homogenizing the curing of the 25 mm thick glass/epoxy composites manufactured by vacuum assisted resin transfer molding (VARTM). The system has a computer-based controller with data acquisition system. The experimental temperature distribution through the thickness of the laminates was compared with a numerical model for both oven and microwave processing. By making use of the computerized insitu temperature-monitoring system, Thostenson & Chou managed not only to adjust the power of the cavity, but also to prevent the temperature lag between the furnace and the composite part. Furthermore, the model adequately simulated the curing process and close agreement was observed with the experimental part. By inverting the Power Vs time graph of the cure process, Thostenson & Chou (1997) found that this graph resembles an isothermal DSC thermogram [Figure 3.4]. The last remark of this recent work is that the main objective was to cure successfully a glass fiber reinforced epoxy. Numerical modeling of electromagnetic distribution was used to assure inside-out curing rather than the conventional outside-in curing of thermal energy. The advantage of inside-out curing, as was mentioned in chapter 2, is the reduction in internal stresses which could lead to cracking in severe heating rates.

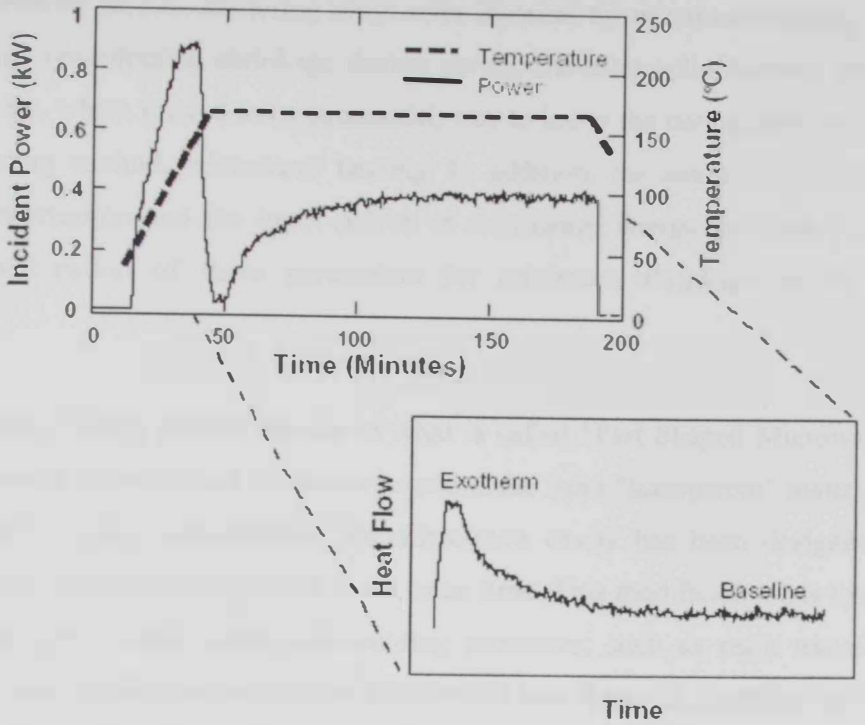

Figure 3.4: Microwave Power applied by the feedback controller in the cure cycle

Wallace et al. (1999) cured a commercial resin system using both thermal and microwave heating. For thermal curing, samples were produced in a conventional oven via isothermal cure at 160 °C for 90, 100, 130, 160 and 180 minutes. The cure schedule for microwave curing was 180 minutes at approximately 40 W followed by 0, 5, 7.5, 10 and 15 minutes at approximately 400 W. The cured resin has been compared using modulated differential scanning calorimetry DSC, dynamic thermal analysis DTA, infrared spectroscopy IR, and solid state NMR spectroscopy. IR and NMR indicate that epoxy-amine reaction is more dominant in microwave curing. DMA graphs suggest difference in network structure as peaks distribution is different in both methods. DSC indicates higher T_g for microwave method with the span between the onset and endset broader than thermal method.

Shull et al. (2000A & 2000B) tackled the issue of material degradation as a result of exothermic reactions of cure. Temperature distribution was obtained during microwave processing from a series of thermocouples embedded at various lateral locations relative to the microwave source and uniformly through the thickness of the composite structure. By careful monitoring of the rapid changes in temperatures through the thickness of the material, more control over thermal runaway and large heat exotherm is achieved.

Ku (2003) worked on manufacturing vinyl ester material by microwave curing. Vinyl ester resins undergo considerable shrinkage during curing and after solidification. Therefore, the approach of Ku, which proved to be successful, was to lower the curing time by using a more efficient heating method, microwave heating. In addition, the amount of initiator used to initiate polymerization and the input power of microwave energy are varied to obtain an optimum combination of these parameters for minimum shrinkage of the composite components.

Zhou & Hawley (2003) reports the use of what is called "Part Shaped Microwave Cavity". Instead of using a conventional microwave mold made from "transparent" materials, such as Teflon, quartz, or pure polyethylene, the microwave cavity has been designed to be the resonance cavity and the casting mold at the same time. This modification has found feasible application in some liquid composite molding processes, such as resin transfer molding (RTM). The main reason behind this modification is that the mold materials do not possess the mechanical properties to maintain integrity for any cyclic RTM process using pressure. A rectangular brass part-shaped cavity was designed instead to withstand high injection pressures while maintaining structural integrity.

3.2.3.3 Mechanical Properties

Mechanical properties of polymers and composites such as tensile strength and modulus, and flexural strength, have been investigated by several researchers in the last few decades. In fact, enhancement of these properties is the most anticipated and yet debated issues in mechanical properties. Since it is also one of the most vital areas of concentration in this research we shall try to summarize the current findings in this area.

During the pultrusion process which has been explained above, microwave radiation was also utilized for drawing polymer based fibers, poly(oxymethylene). By using the microwave energy instead of the thermal one, not only the draw ratio increased from approximately 20: 1 to 35:1 but also a corresponding increase in the modulus from 35-40 GPa to 55-60 GPa were found (Nakagawa et al., 1983; Takeuchi et al., 1985; Nakagawa et al., 1985). It was found that the increased orientation of the polymer chain in the fiber direction is the main reason for increased strength. It is worth while mentioning that Lewis et al. (1987) were also one of the

pioneers to call for the need of more comprehensive examination of the chemistry of the cure. In addition, he called for more systematic mechanical testing of microwave processed samples.

Microwave energy is reported as a means of preheating sheet molding compounds (Costigan et al., 1988). The rapid heating feature of microwave energy reduces thermal gradient and improves flow in the mould. In addition minimum fiber orientation and more uniform mechanical properties were achieved.

Singer et al. (1989) carried out another interesting study. They found that the tensile strength of the microwave specimens below 80% degree of cure was significantly lower than thermally cured specimens. As the extent of cure increased, the tensile strength of the microwave specimens improved, and at 100% degree of cure the mechanical strength of the microwave cured specimens surpassed the thermally cured ones. In addition, the modulus of elasticity was slightly higher in the microwave-cured specimens. Singer et al. also explained the low tensile strength at the low degree of cure due to less molecular entanglement of the polymer network due to alignment in the electric field (Thostenson & Chou, 1999). For the same value of Young's modulus in a thermal and microwave cured resin, they also found out that the microwave one has less deformation resistance due to existence of micro cracks in the microwave sample.

Early work by Hedrick et al. reported drastic drop in cure time for epoxy resin thermoset (Hedrick et al., 1991). In this work, a controlled electromagnetic field in a single-mode microwave applicator was utilized to cure epoxy resin. Fully cured networks, monitored by DSC, were obtained with high time reductions. The time reductions reached nearly ten minutes compared to three to four hours in thermal cycles.

Boey et al. (1991) used an electromagnetic source to cure glass fiber/epoxy composites using vacuum bagging technique. The metallic tooling was replaced by low loss material to prevent electromagnetic interference and overheating. A 0/90 continuous cross woven fiber E-glass fabric was used. Samples cured at 400, 600, and 800 watt respectively were mechanically tested using a standard four point bending test. For lowest power setting, the results indicate that the maximum strength and moduli values were achieved in less than 20 minutes compared to at least 8 hour for thermal curing. In the 600 watt power setting, the maximum

strength was achieved at 12 minutes only. However, at the highest power rating, 800 watts, the strength increased after short time, about 6 minutes, and then started to decrease. Boey et al. suggest thermal degredation took place at this high power rating since initially the loss factor is high for epoxy and increasing and extensive amount of energy is absorbed. In general, the maximum strength achieved for Boey's work agrees with the findings of Singer et al. (1989).

Mechanical properties of glass/vinyl ester composites, measured by Remarkrishma et al. (1993), were shown to be at least equivalent to those of conventionally processed materials, with indication that some property enhancement attributed to reduced void content occurred. In addition, enhanced adhesion was observed for carbon-fiber composites due to preferential heating at the conductive fiber surface (Drzal et al., 1991). This remark is due to the high energy reflectivity of the carbon fibers which will heat the surrounding resin and result in more rigid bonding and thus higher strength.

Gaskin et al. (1993) has similar work on lap shear joined by adhesive bonding. Three adhesive systems with different cure temperatures 121 °C, 177 °C, and 149 °C were analyzed. In general, the mechanical properties were slightly lower in the microwave cured specimens. Voids formation due to trapped volatiles is suggested as an explanation to these results. The author then concludes that by modifying the formulation of the adhesive more efficient curing could be achieved through microwave curing.

Denture acrylic resins are also tested under microwave energy by Diwan et al. (1993). Specific processing recommendations were suggested to assure adequate and comparable properties to conventional curing methods. First, a sufficient pressure should be maintained on the material to prevent voids. Second, aggressive or rapid heating must be avoided initially to avoid gaseous porosity resulting from volatile components. Finally, all metallic components such as flasks or flask clamps must be carefully insulated to prevent arcing when exposed to microwaves.

Jordan et al (1995) compared the thermal and microwave property of epoxy/amine mixtures. Samples cured by both thermal and microwave processing were characterized by dynamic and static mechanical properties and then compared with those of fully crosslinked networks,

postcured at a high temperature. No changes were monitored in the elastic properties between two methods.

Paulauskas et al. (1996) tested the shear behavior of single lap adhesive joint, in both microwave and conventional curing. The shear strength was found to be comparable in both cases. However, the ultimate tensile strength for the microwave processed samples was slightly higher than for conventionally cured samples.

Thostenson & Chou (1999B) examined microwave heating as an alternative to conventional heating for joining of composite structures. Rapid and selective heating advantages of microwave curing were utilized in heating interlayer epoxy paste material that has high dielectric loss properties relative to the substrate material. Both conventional and microwave curing methods are mechanically compared by shear testing. Microwave curing resulted in both enhanced shear strength and less scatter in experimental data.

Rahmat & Day (1999) reports the use of microwave heating in resin transfer molding (RTM) to fabricate both neat polyester resin and polyester/aramid composites. Special Teflon molds are manufactured to accelerate the process by maximizing the amount of energy absorbed by the resin. Flexural modulus and strength of the composite samples obtained using microwave heating were higher than those of thermally cured composites.

Fang et al. (1999) investigated the application of microwave energy to the processing of carbon fiber reinforced polyimide composites with a variable-frequency microwave furnace (VFM). The mechanical properties were determined by 3-point-bending and short-beam-shear tests at both room temperature and 177 °C. Higher flexural strength, flexural modulus, and shear strength at 177 °C were observed for microwave method with curing time one-half the thermal method.

Muhtarogullari et al. (1999) carried out another work considering the curing of PMMA dental base material. Dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), thermogravimetric analysis (TG), and thermal analysis were carried out. Regarding the mechanical analysis, the movement of molecular chains was represented in (DMA) in the form of variation of different mechanical properties with temperature changes. Higher mechanical properties were observed for microwave curing. For the other tests, the glass

transition temperature T_g measured (about 110°C) by DSC increased with curing period in microwave oven.

Yunchang & Hawley (1999) used a computer controlled variable frequency microwave (VFM). 24 ply of unidirectional carbon fiber/epoxy prepreg was cured using a developed smart code to improve the heating uniformity and curing temperature stability by intelligently adjusting the frequency and power. Heating results demonstrated the efficiency and stability of the control system. Flexural tests on samples heated for 90 minutes showed improved product quality resulted from decreased temperature gradients.

Zhou et al. (2000) compares the mechanical properties of E44 commercial epoxy resin cured by different percentages of maleic anhydride curing agent. The observed development in mechanical properties in the microwave case was stated, as explained previously, in light of the homogeneity of the cure.

Variable frequency microwave (VFM) is again used by Tanikella et al. (2002) as a rapid curing alternative for the processing of polymer dielectrics, commonly used in microelectronics industry. The electrical, optical, mechanical, and chemical properties were characterized and compared with thermally processed films to determine the effectiveness of microwave processing. The microwave properties were found to be comparable to thermally cured ones with high reduction in total curing time.

Nightingale & Day (2002) had also some controversial results. They tested the flexural strength and modulus of carbon fiber/epoxy composites for both thermal and microwave based methods. The setup used is a commercially available microwave with five power settings. The pulsed system consisted of power-time cycle where the power is shifted off and on for different period of time. The overall power delivery then can be averaged according to the total time "on" with respect to total time of operation. This is the common system used in commercial home-use ovens. A vacuum bag is used only in oven curing while in microwave curing it was not possible. The high reflectivity of carbon fibers generates sparks which tear the bag and loose the pressure. Instead, less efficient clamps of Teflon were used to hold plys together resulting in increase of void content. Three groups of carbon fiber/epoxy composites were prepared, Oven curing, partial oven curing followed by microwave post-curing, and full microwave curing. The outcome of the research stated that oven curing produced higher

flexural properties and interlmainar shear strength than the partially microwave system. For the third group, microwave curing, properties were similar to the oven cured ones. This result was not expected as the microwave cured samples were not processed under vacuum. However, Nightingale and Day explained this by stating that better adhesion between the fiber and the matrix due to the reflected heat from carbon fibers could be responsible for this result. The effect of cure time was surprisingly found to be negligible. Time durations of 5-40 minutes resulted in similar mechanical properties. The effect of carbon fibers on the amount of heat generated is more dominant on the contrary to fiberglass. Also the effect of aligning the specimen inside the cavity was also negligible.

In the field of dental science, Usanmaz et al. (2003) have recent work to compare the thermal and mechanical properties of PMMA dental base material cured by microwave and conventional heating methods. The materials were cured with a boiling water temperature and microwave radiation for periods of 5, 10, 15, 20, 25, 30, and 35 min for thermal curing, and 1, 2, 3, 5, and 7 min for microwave radiation. The mechanical properties of the samples were determined from tensile and three-point bending tests. The elastic modulus was highest for samples obtained by the conventional method with a 30-min curing period while the bending modulus was highest for 7-min cured samples in a 700-W microwave.

Rahmat et al. (2003) worked on the microwave curing of unsaturated polyester in comparison to conventional curing method. It was found that the shear modulus, flexural modulus, and flexural strength were not significantly different. In addition, solid state NMR supported the mechanical properties by showing similar spectra for both microwave and thermal cured samples. This suggests the same network formation and chemical reactions in both cases.

Zhou et al. (2003) studied the effect of curing agent percentages on the mechanical properties of epoxy resins. Instead of using the recommended phr (part per hundred) of the curing agent, they started varying the phr from 25-40 %. The compressive and bending strength measured by thermal and microwave methods indicate significant increase of mechanical properties as the curing agent percentage is increased. The increase in microwave samples was found to be higher than thermal cured samples. The research explains this phenomenon indicating, first, more homogenous heat delivery in the microwave case. Same results and explanations were recorded by Bai et al. (1995). Second, the microwave cure promotes the polymerization of the epoxy resin, checks some side reactions, and makes the molecular packing more compact.

The authors however did not provide an experimental verification for their findings particularly crucial to support their claims. They also indicated that the curing temperature in microwave curing was reduced by 15-20 °C from thermal curing without indication of the criterion by which they have selected this optimum temperature of cure. In other words, other cure temperatures should be checked to support the temperature reduction claim.

One of the latest works in mechanical properties of composites was carried out by Hubbard et al (2004). They studied the effect of microwave cuing on the mechanical properties of polyimide wafer coatings, a common material in electronic chips industry. The thermal curing by convection at higher temperatures, 350-400 C, was found to change the electrical properties of the devices. The work describes the use of variable frequency microwave (VFM) for the curing of existing polyimides at more than 50-150°C lower than the standard convection cure temperatures while maintaining the necessary final mechanical and chemical film properties.

Yarlagadda & Hsu (2004) studied three types of epoxy resins which are commonly used for making injection moulds. Tensile and flexural strength were measured to compare the thermal and microwave processing methods. Most of the microwave cured samples have at least reached the manufacturer recommended strength and sometimes exceeded these values depending on the hardener used. The glass transition temperature, measured by DSC, was found to be higher for microwave heating, especially desirable for mold manufacturing. The examining of fracture surface microstructure by SEM, however, indicated high amount of processing cavities. This was suggested as the reason of rupture of some samples while subjected to loading. This fact has lead to not using the data of at least 5 successful samples per set, recommended by ASTM testing standard.

3.2.3.4 Microwave Effects

One of the most debated issues in microwave processing of thermoset is what is known to be the "microwave effects". The most critical of these effects is the effect on reaction kinetics. Many researchers claim that microwaves accelerate reaction kinetics while others disagree in other researches. In other words, some researchers claim that the main reason behind microwave rapid heating is not merely direct transfer of energy. The main cause, in their opinion, is that the cross linking rate is higher in microwave or the chemical reactions themselves. Merand et al. (1992), Wei et al. (1993), Jordan et al. (1995) and Parodi (1999) have studied the cure kinetics of epoxy resin systems. They concluded that the reaction rates were enhanced and times to gelation and vitrification were reduced.

Mijovic and co workers (1998) have claimed the opposite. They found no change or even retardation in curing kinetics. Their approach was to use an FTIR device to insitu monitor the disappearance of epoxy functional groups during curing. They found that the rate of disappearance is identical for both microwave and thermal curing. The total curing time was also found to be the same. This work has strongly affected the concept of microwave effects. The approach of insitu monitoring of the behavior formed an effective analysis tool.

Rahmat & Day (1999) cured samples of neat polyester and polyester/aramid composites in a microwave resin transfer molding (RTM) process and compared them to thermally cured ones. Fourier Transform Infrared Spectroscopy (FTIR) was used to produce plots of styrene vinyl conversion versus polyester vinyl conversion for both microwave and oven curing. The identical behavior of both curing methods suggests that the reaction mechanisms for materials prepared by the two routes are similar which again disagree with the "non-thermal effects" of microwave energy.

A recent work by Hawley (2001) has further discussed the issue of microwave effects. Two issues have been tackled, acceleration of curing kinetics and the localized superheating phenomenon of some side groups of the polymer chain. To determine if there is "non-thermal effects" of microwave processing, comparative study of pulsed-power and continuous-power microwave curing of epoxy systems was carried out. The main difference between both is that pulsed-power microwave switches on and off in a specific time period to control the power

delivery while the continuous microwave controls the actual power rating (Watts). More explanation can be found in section 4.2.1. If non-thermal effect is the main reason of microwave enhancement of reaction rates, then continuous-power curing will have faster reaction rates than pulsed-power curing. Experimental results showed that continuous-power curing had only slightly higher reaction rates than pulsed-power curing. From the first look this result seems to disagree with the "microwave effects" theory. However, there are two factors that may have led to the non-significant enhancement of continuous-power curing over pulsed-power curing, the power levels and the pulse cycles. The incident power for pulsed-power curing was around 43 watts while the incident power for the continuous-power curing was lower than 25 watts. This means that the pulsed-power curing has a much stronger electric field. Therefore, when the power was turned on, the pulsed-power curing had a much higher heating rate than continuous-power heating. This conclusion calls for additional work unifying the output power of both the pulsed and continuous microwaves. A microwave thermal-mechanical analysis (TMA) system was also built to inspect the phenomenon of localized superheating. By comparing TMA data of both thermal and microwave curing, similar relationships between T_g and curing times were observed which makes the phenomenon of "localized superheating" questionable.

Zhou and Hawley (2003) also have studied the reaction rate enhancement on adhesive bonding of both polymers and composites. They accounted the enhancement in cure rate due to localized superheating of functional groups. Since carbon black powder has high affinity for absorption of microwave energy, the approach was to add carbon black into epoxy to modify microwave thermal effect without significantly affecting the non-thermal alignment of polar groups in the electromagnetic field. In microwave curing, microwaves are absorbed by the functional groups, dissipated into heat and then the heat is transferred to the entire molecules. When carbon black is filled into the resin, most microwaves are absorbed by carbon owing to its much higher dielectric property. Heat is then transferred from carbon to the resin molecules and the functional groups of the resin. They have verified their hypothesis by proving that the rate of cure gradually decreases by adding the carbon black. Degree of cure was measured by taking samples of the resin during cure and testing it using differential scanning calorimetry DSC.

3.3 Conclusion of Literature Survey

We can observe from the literature review carried out several remarks. First, in order for us to improve the properties of glass reinforced composites, researchers have focused on improving and understanding the behavior of the thermoset resin itself. Main reason for that is the low dielectric property of glass fibers on the contrary of carbon fibers. Second, although thermoplastics and some thermoset resin like polyester, PMMA, Polyurethane, and vinyl ester have also been investigated, most of the efforts are dedicated to DGEBA epoxy resin. This is due to the fact that long time required in thermal curing curbs the spreading of this type of resin. An efficient less time consuming method has to be developed. Third, researchers in mechanical properties have been subdivided into two groups. An "optimistic" group believes on the superiority of microwave mechanical properties, while the other group at least agrees on the compatibility of both thermal and microwave curing methods. Yet, both groups agree on the reduction in cure time. Fourth, design of more process control systems and efficient microwave applicators could provide more resources on the cure cycle monitoring and control. "Blind" processing of polymers and polymer composites will definitely result in defected products. Fifth, some observed properties, such as "microwave effects", are still a source of debate between researchers. The microwave effects dilemma is more complicated since the comparison of contradicting researches is difficult. The difficulty here is due to the fact that each researcher is working on different materials and using different methods of measuring cure kinetics. Carrying out further studies unifying the material and method of application can definitely solve this issue. Sixth, more analytical methods have to be developed to insitu monitor the structural changes on the molecular level. This is, in my opinion, the best method to solve the current debate over the microwave material interaction.

Chapter 4

MATERIALS & EQUIPMENT

Chapter 4

Materials & Equipment

4.1 Materials Specifications

4.1.1 Epoxy Resin

In this section we will adequately characterize both the polymeric resin and the reinforcement matrix. The characterization will include supplier information and specifications, mix ratios, and pre-testing conditions. The resin chosen is a modified Diglycidyl of Bisphenol A (DGEBA). The resin is supplied from Dow Chemicals as DER324 and used as received. The commercial resin in itself is a formulated blend of DER331 (DGEBA) and a reactive diluent C_{12}-C_{14} aliphatic glycidyl with a blend ratio of 83/17 respectively [Figure 4.1].

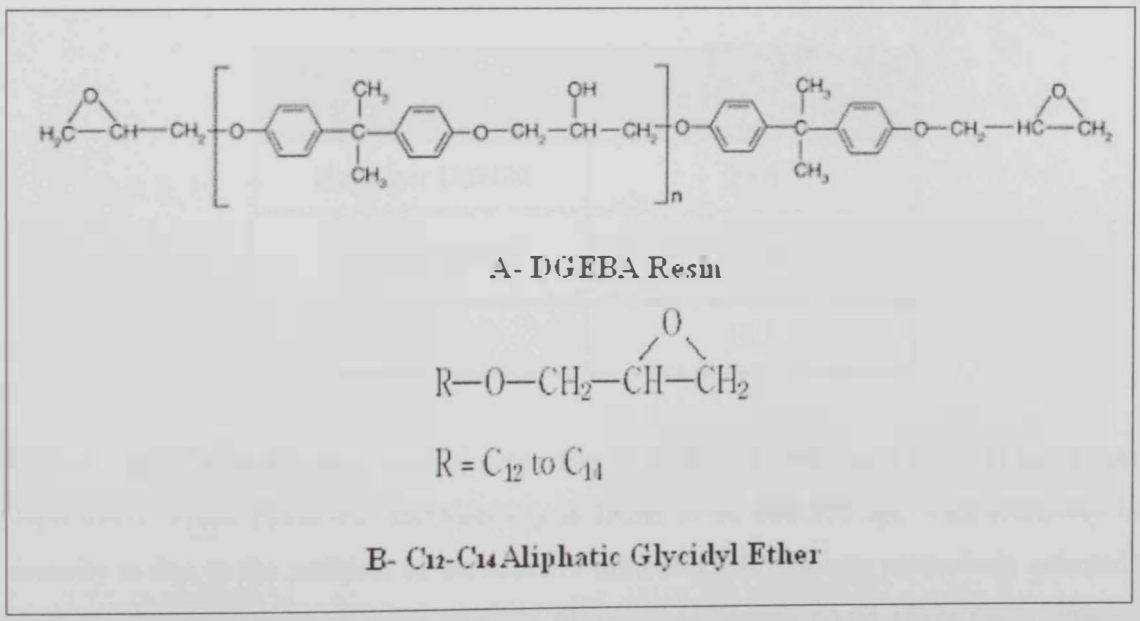

Figure 4.1: Structure of DGEBA (A) and C_{12}-C_{14} Aliphatic Glycidyl Ether (B) (Dow, 1999)

Common applications of this resin are flooring compounds, grouts, adhesives, decoupage coatings, high solids coatings, and composites. In order to reach optimum properties, a curing agent must be used to build a three dimensional, thermoset network. Diethylene triamine (Dow DEH20) is chosen for this cross linking operation. Stoichiometric Ratio of mixing was calculated based on the following equation (Dow, 1999):

$$Phr\ of\ hardner = \frac{Hardner\ \ Eq.wt\, X\, 100}{Epoxide\ \ Eq.wt\ of\ resin} \qquad (4.1)$$

Where

Phr : Parts -by weight- per 100 parts resin.

Eq. wt : Equivalent weight, in grams, calculated by dividing the molecular weight of the resin by the number of active hydrogen in the chain

Table 4.1 shows that the epoxide equivalent weights for hardener and epoxy are 20.6 g & 200 g (average) respectively. Epoxide equivalent weight is defined as the weight in grams which contains one gram equivalent of epoxide (Encyclopedia, 1985). The final stoichiometric ratio was found to be 10.3:1. This means that for each 10.3 grams of epoxy resin one gram of hardener is mixed to produce a reactive curing resin.

Table 4.1: Calculation of Stoichiometric Ratio (Dow, 1999)

Material	Equivalent wt. (g)
Hardener DEH20	20.6
Epoxy DER324	197-206
Phr	10.3

Table 4.2 and Table 4.3 show typical properties of DER 324 resin and DEH 20 curing agent, respectively. From Table 4.2, the viscosity is found to be 600-800 cps. This relatively low viscosity is due to the addition of the reactive diluent. DER 324 was particularly selected to avoid any heating necessary prior to mold filling. This heating could affect the accuracy of

cure detection. In Table 4.3, the suggested cure schedule is mentioned according to Dow Company. This schedule will be taken as a cycle design guideline in the experimental results.

4.1.2 Reinforcement Material

In composite samples, unidirectional strand rovings of E-glass fibers are used as reinforcement. The fiber glass uniweave laminates is used as sheets to be cut in specified mold dimension and used as received. The glass fabric laminate has a surface density of 435 g/m^2.

Table 4.2: Physical properties of DER 324 epoxy resin (Dow, 1999)

Resin	Viscosity Range (cps @ 25°C)	Specific Gravity, 25/25°C	Weight (Lbs/Gal) @ 25°C
D.E.R. 324	600-800	1.11	9.3

Table 4.3: Curing Behavior of DEH20 curing agent (Dow, 1999)

Curing Agent	Phr D.E.R. 324	Suggested Cure Schedule	Comments
D.E.H. 20	10.3	Gel at RT plus several days at RT or 1-2 hrs at 100°C for full cure.	General purpose RT curing agent. High exotherm in large mass. May blush under humid conditions.

4.2 Experimental Setup

4.2.1 Microwave Processing System

The microwave processing system was the product of six month market survey. The objective of this survey was to study, compare, and analyze various types of microwave processing systems. Single mode vs. multi mode, continuous vs. pulsed power delivery, fixed frequency vs. variable frequency, are some of the comparison aspects on which the final selection was based. Many Microwave manufacturers were contacted such as Lamda® Autowave® series, Fricke & Mallah®, Richardson Electronics®, Cobber Muegge®, Unique Broad Band systems UBS®, RADATHERM®, and many others. In addition, numerous temperature measurement tools were evaluated such as thermocouples, fiber optics, and pyrometers. Even dielectric measurement tools such as dilectrometric sensors, and network analyzers were studied. Based on received quotations, the sample sizes, the time available for testing, required mode of propagation, the accessibility of experimental measurement tools, and most importantly the project budget, an assembled setup from Fricke and Mallah® was selected. The company has provided us with a specially tailored system to match the current and future research plans in UAE University. The system was designed to assure maximum efficiency of heating.

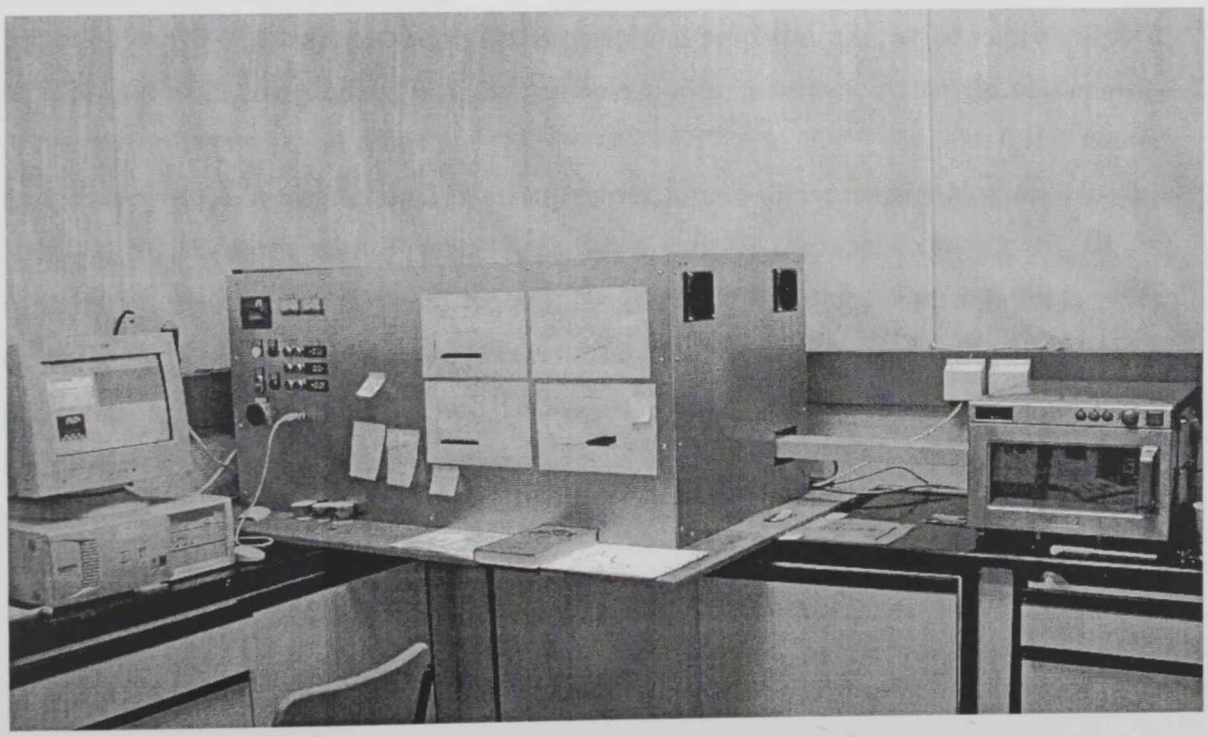

Figure 4.2: Overview of MW Processing system at UAE University

Figure 4.2 and Figure 4.3 present an overview of the chosen system. The following is a description of this system:

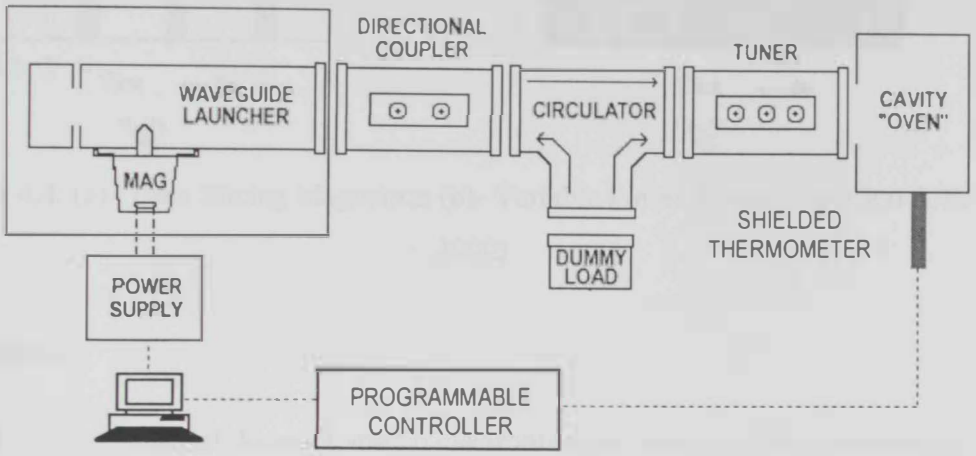

Figure 4.3: Schematic Diagram of the Microwave Processing system

A- 1.9kW-Microwave-Generator

The main component of the generator is a water-cooled 1.9kW multi mode magnetron with a fixed frequency of 2.45 GHz. Multi mode magnetron is needed to assure homogenous microwave distribution in the cavity. The magnetron is protected against thermal overload by a thermal switch. The output power of the magnetron is proportionally varied from 0 to 100%. It is worth while mentioning that the variable power generator system is conceptually different than the home use generator which works on "time slicing" principle. If it is desired to operate a 1000W generator on 25% of full power, a time slicing magnetron applies the full 1000W for 25% of the time, Figure 4.4a, while a variable one applies only 250W for the desired time duration, Figure 4.4b (Chai & Riley, 2000). This real time control raises the price of the magnetron tremendously. However, the increase in price is reflected in better performance. It is evident that the variable power microwave produces higher reaction rate for epoxy resin than the pulsed power system and at the same time more control over the cure cycle is achievable (Bao & Hawley, 2000).

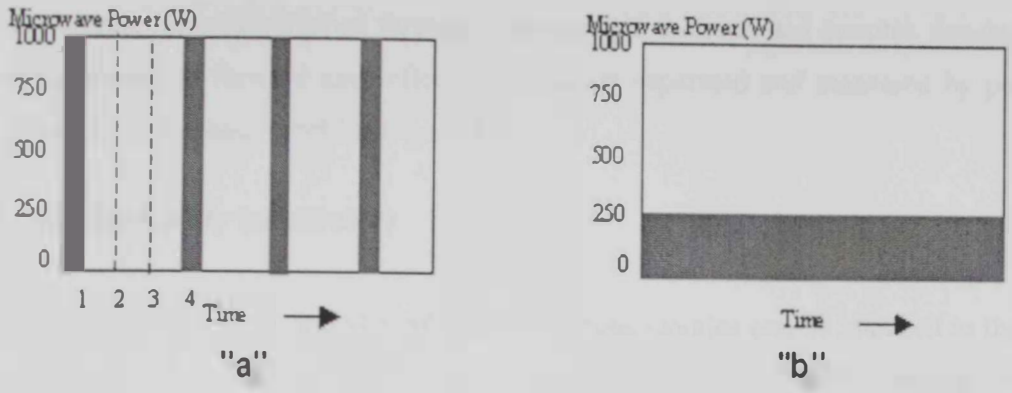

Figure 4.4: (a)- Time Slicing Magnetron (b)- Variable Power Magnetron (Chai & Riley, 2000)

B- Circulator

In case the heated material does not absorb electromagnetic energy, a huge amount of energy is reflected back. To protect the magnetron against reflection a water-cooled circulator is used. The reflected power is deflected to the matched broadband water load. The water load then dissipates the absorbed heat away. A water cycle is required to continuously exchange the heated water. The reflected power is measured at the water load using the corresponding microwave detector. The value of the reflected power is displayed on analog instrument and can be used for the power matching.

C- 3-Stub-Tuner

For the power matching a 3-Stub-Tuner is used. Each stub is derived by an electrical motor. The penetration depth of every stub into the wave guide can be varied manually until the reflected power P_r reaches a minimum. The position of every Stub inside the wave guide is digital displayed. Only the power matching between the microwave generator and the heating cavity (applicator) guarantees a rapid and efficient heating of the probe placed in the cavity [Figure 4.5].

D- Directional Coupler

Since the ability of materials to absorb electromagnetic energy depends on the dielectric properties, the amount of power absorbed and reflected will be a feasible estimate. Power

measurement is accomplished through a device called directional coupler, designed so that a small amount of forward and reflected waves are separated and measured by power meters (Thostenson & Chou, 1999A) [Figure 4.5].

E- Heating Cavity (applicator)

According to the shape and size of samples various cavities can be attached to the generator. For our sample size, a professional microwave cavity was used with rotating fan or "mode stirrer" to produce even microwave fields [Figure 4.6]. This oven is adapted on one side of the cavity enabling the connection with the generator waveguide. For temperature measurement a shielded platinum resistance thermometer, Pt100, is used. In case a conventional thermocouple is used, significant electromagnetic interference may occur. Therefore, a shielded thermometer is necessary to prevent the electric field from concentrating at the probe tip [Figure 4.7].

F- Control Unit

All devices necessary for operation and monitoring are located on the front panel of the system. The operation and alarm conditions of stub tuner motor drives and microwave generator are displayed. Specific cure cycles can be programmed by the programmable controller so that the process parameters are adjusted to satisfy the planned cure cycle [Figure 4.8].

G- Process Control & Data Acquisition Software:

A fully configurable, high accuracy process controller is used to control the curing process. The controller is supplied from Eurotherm®. A maximum of 20 programs can be designed to achieve specific heating profiles. In addition, dedicated software, iTools® Version 4, was supplied with the system. The software is a useful utility that enables programming, monitoring, and recording the process parameters of the heating process. RS232 connection is used to connect the PC to the data acquisition system. The modes of operation and the control methods will be thoroughly dealt with in the experimentation chapter.

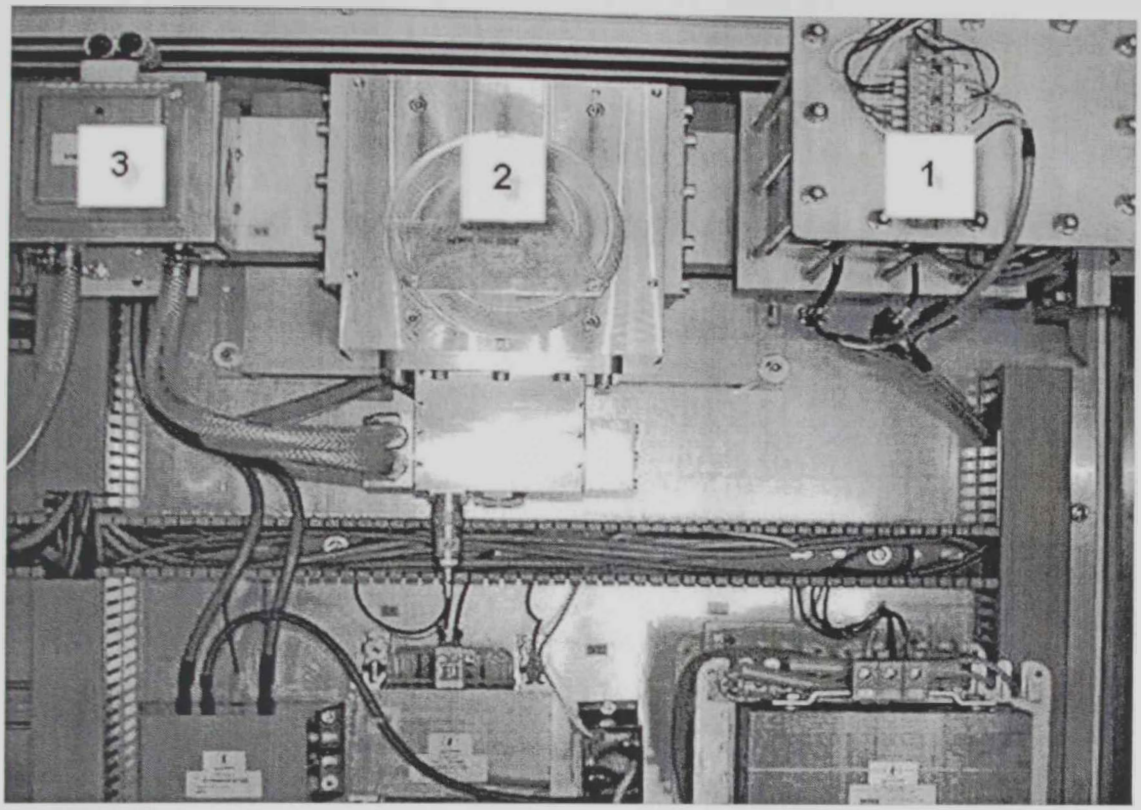

Figure 4.5: Top View of the MW processing system (1) Stub Tuner (2) Directional Coupler (3) Magnetron.

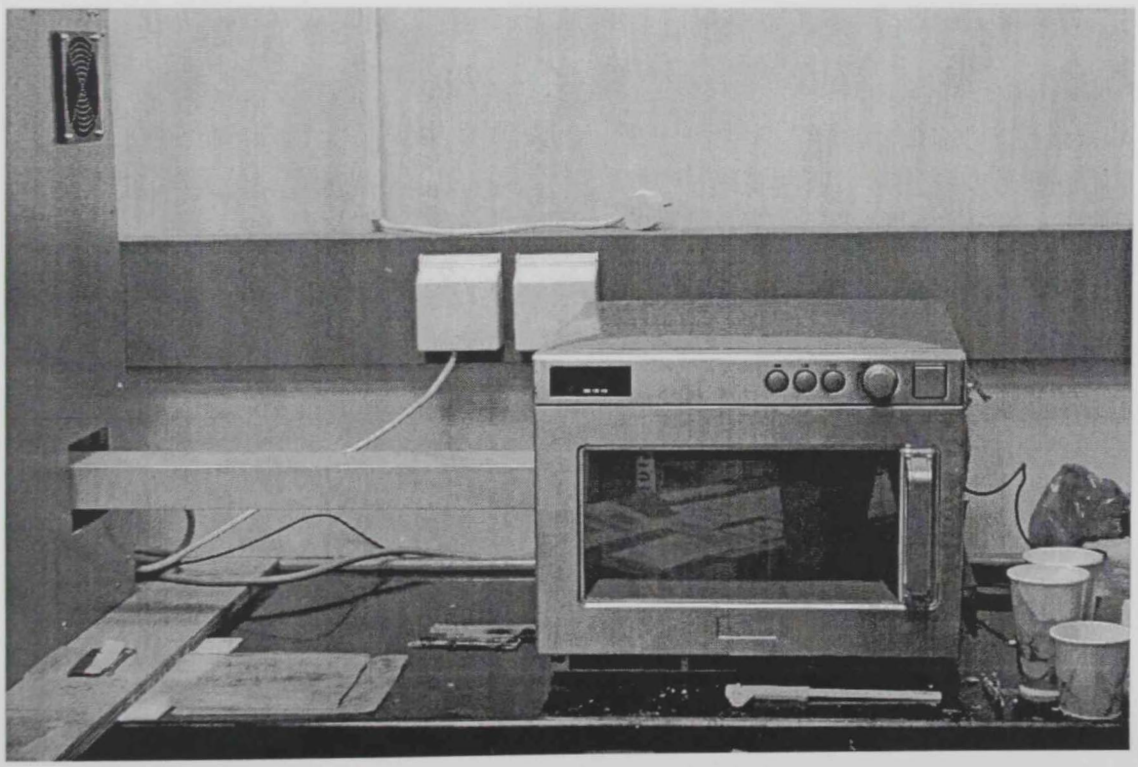

Figure 4.6: Heating Cavity of Microwave Processing System

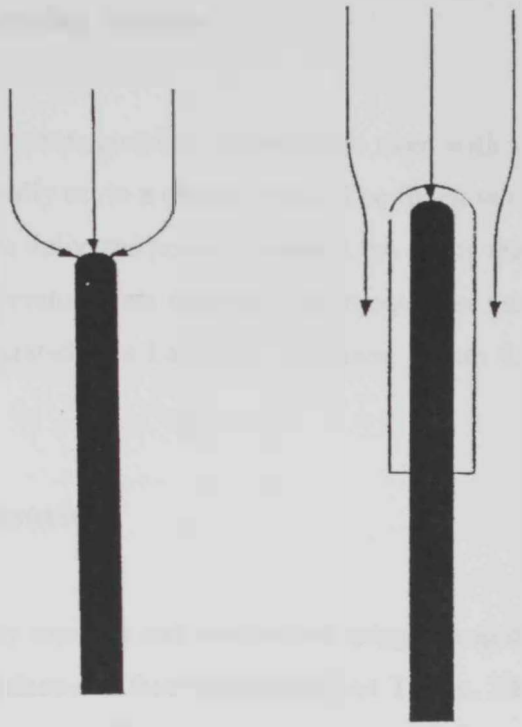

Figure 4.7: Effect of Shielding on the electric field concentration at the probe tip (National Materials Board, 1994)

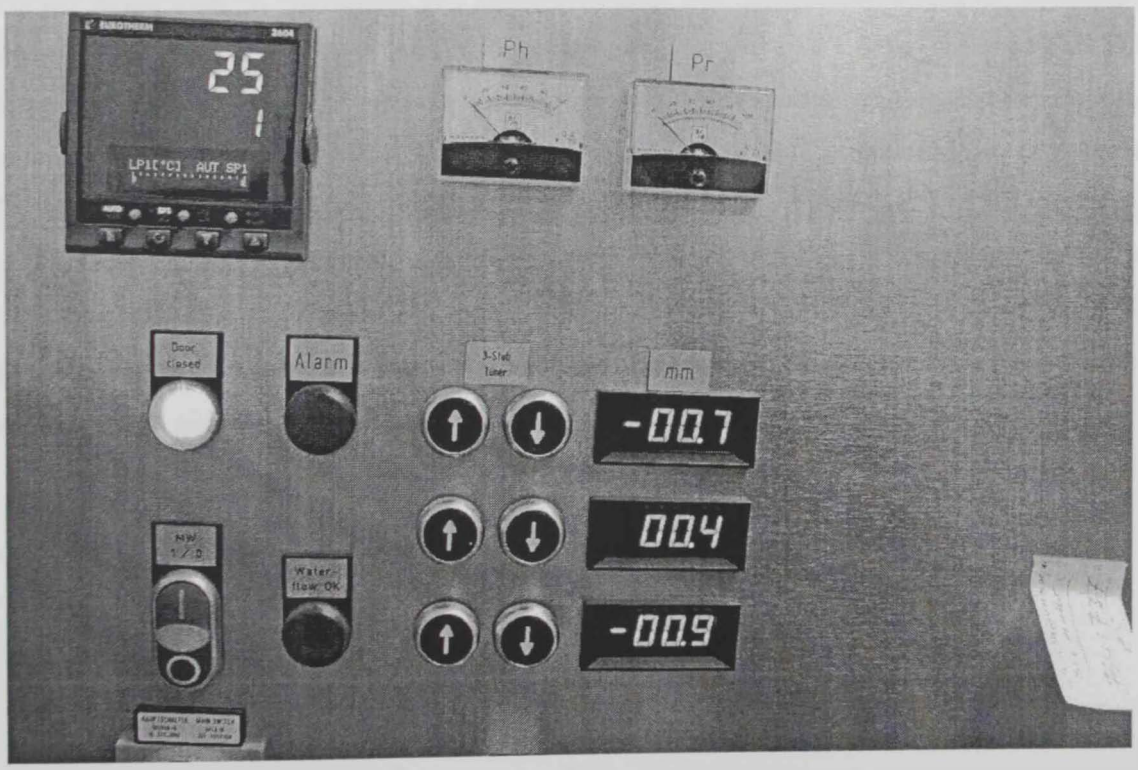

Figure 4.8: Control Unit of Microwave Processing System

4.2.2 Thermal Processing System

The thermal processing system consists of an electric oven with a temperature control gauge. The temperature is manually set to a desired value. The function of the oven controller is then to continuously adjust the delivered power to control the cavity temperature. In addition a data acquisition collects temperature data through 3 thermocouples attached to the oven. The data acquisition system is operated by a LabView® program. Figure 4.9 shows thermal processing setup.

4.2.2 Molds & Accessories

In order to process epoxy samples and composites using lay-up method, two different molds were designed and manufactured from aluminum and Teflon. The aluminium mold is to be used for oven curing while the Teflon mold is to be used for microwave curing. Teflon is considered the most suitable material for microwave processing due to its low dielectric properties, ε'' is around 0.0003. Nearly all the literature work utilizes this material in various shapes and molds. From Figure 4.10 we can see that the Teflon mold (120X20X4mm) is slightly larger than the aluminium one (80X16X4mm). The main reason is that the microwave thermocouple which is 3 mm thick will be inserted into the side of the Teflon mold. This necessitates a larger width to assure more representative temperature reading. Having both the same thickness, however, will make the mechanical testing data comparable to each other. Figure 4.11 shows the detailed dimensions of the Teflon mold. Figure 4.12 is a 3D modelling of the Teflon mold placed on a specially designed Teflon Table. The thermocouple is shown to be inserted from the side of the mold. A more realistic representation is in Figure 4.13. Both the aluminium and Teflon mold had to be waxed with a release agent. The sides had to be sealed with silicon rubber to prevent leakage.

4.3 Analysis Equipment

4.3.1 Differential Scanning Calorimetry

A Perkin Elmer differential Scanning Calorimetry DSC-7 was used to monitor the kinetic behavior of the epoxy resin and to develop the curing model. The power compensation principle mentioned previously is applied in order to carefully measure the heat evolved during the cure cycle of the material. When the temperature rises in the sample material due to exothermic reactions of curing, energy is removed from the cell to compensate for the sample energy. The amount of power required to maintain system equilibrium is directly proportional to the thermal changes occurring in the sample. Sealed Aluminium pans are used for both the sample and reference cells. Calibration was performed using indium and Zinc specimen as reference material with known thermal behavior in order to determine the base line of the machine and assure correct heat flow readings.

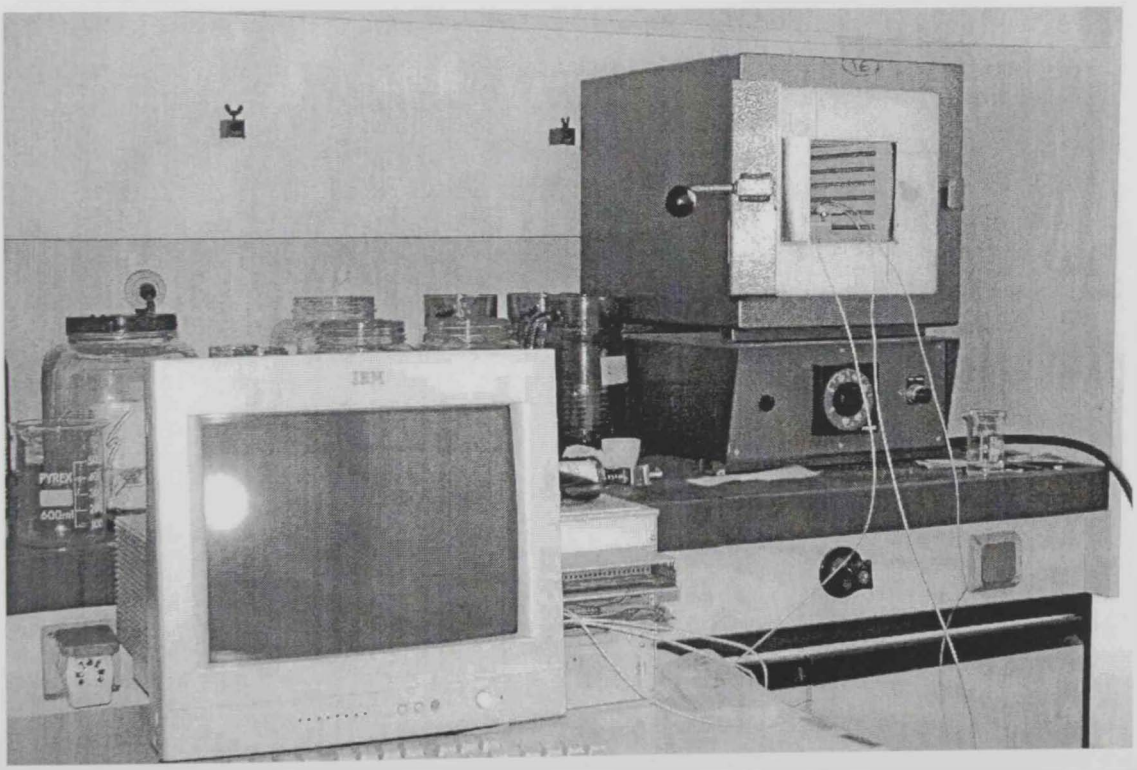

Figure 4.9: Thermal Processing System (Oven)

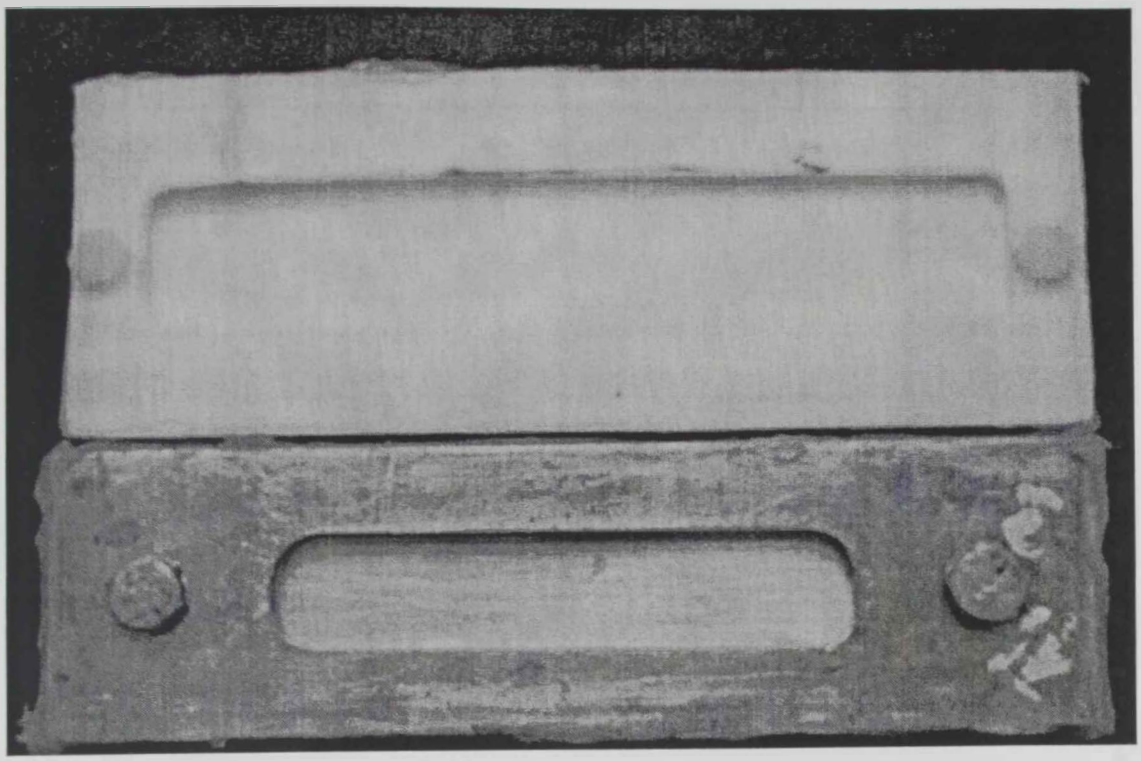

Figure 4.10: Teflon Mold (above) Aluminum Mold (below)

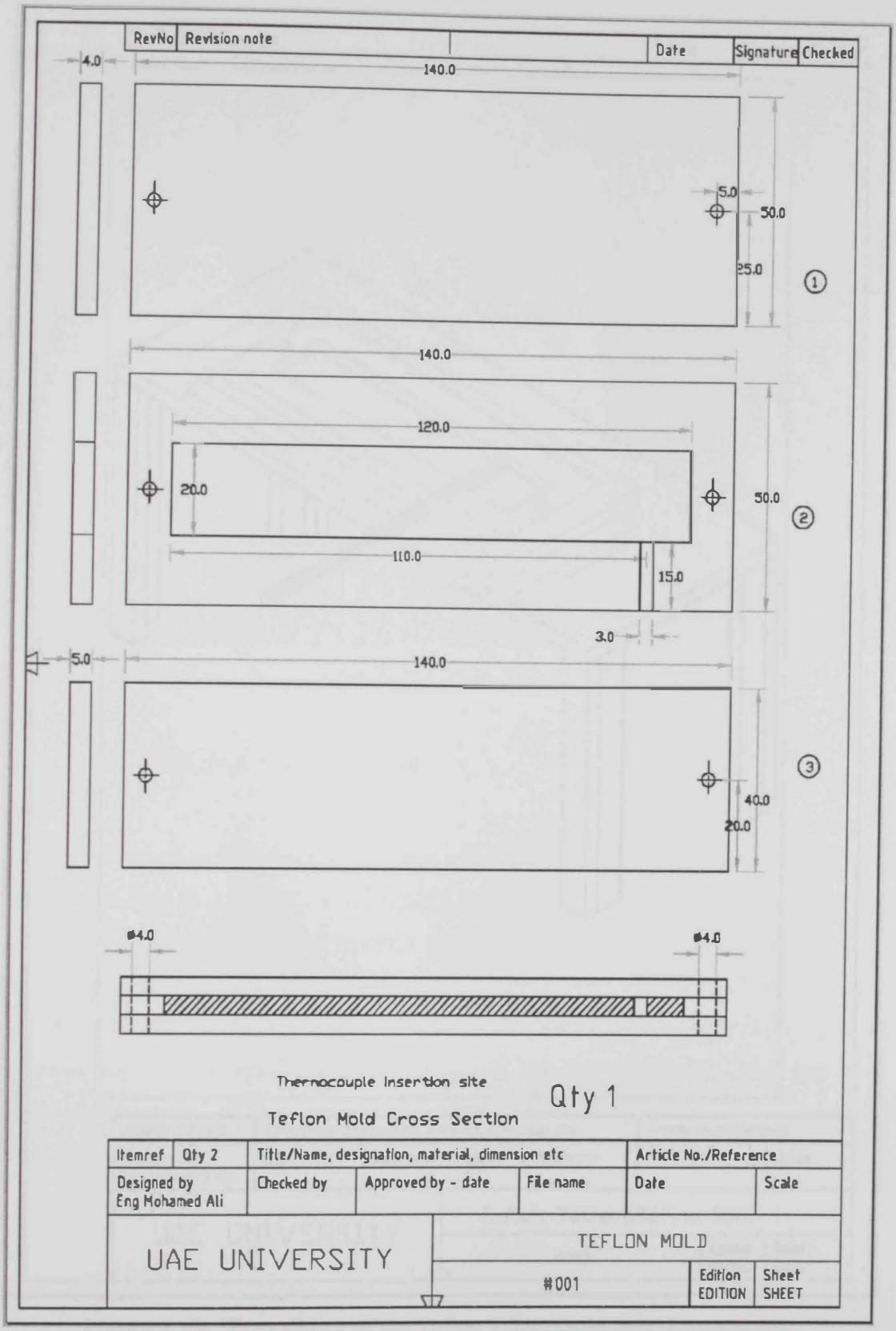

Figure 4.11: Detailed Dimensions of the Teflon mold.

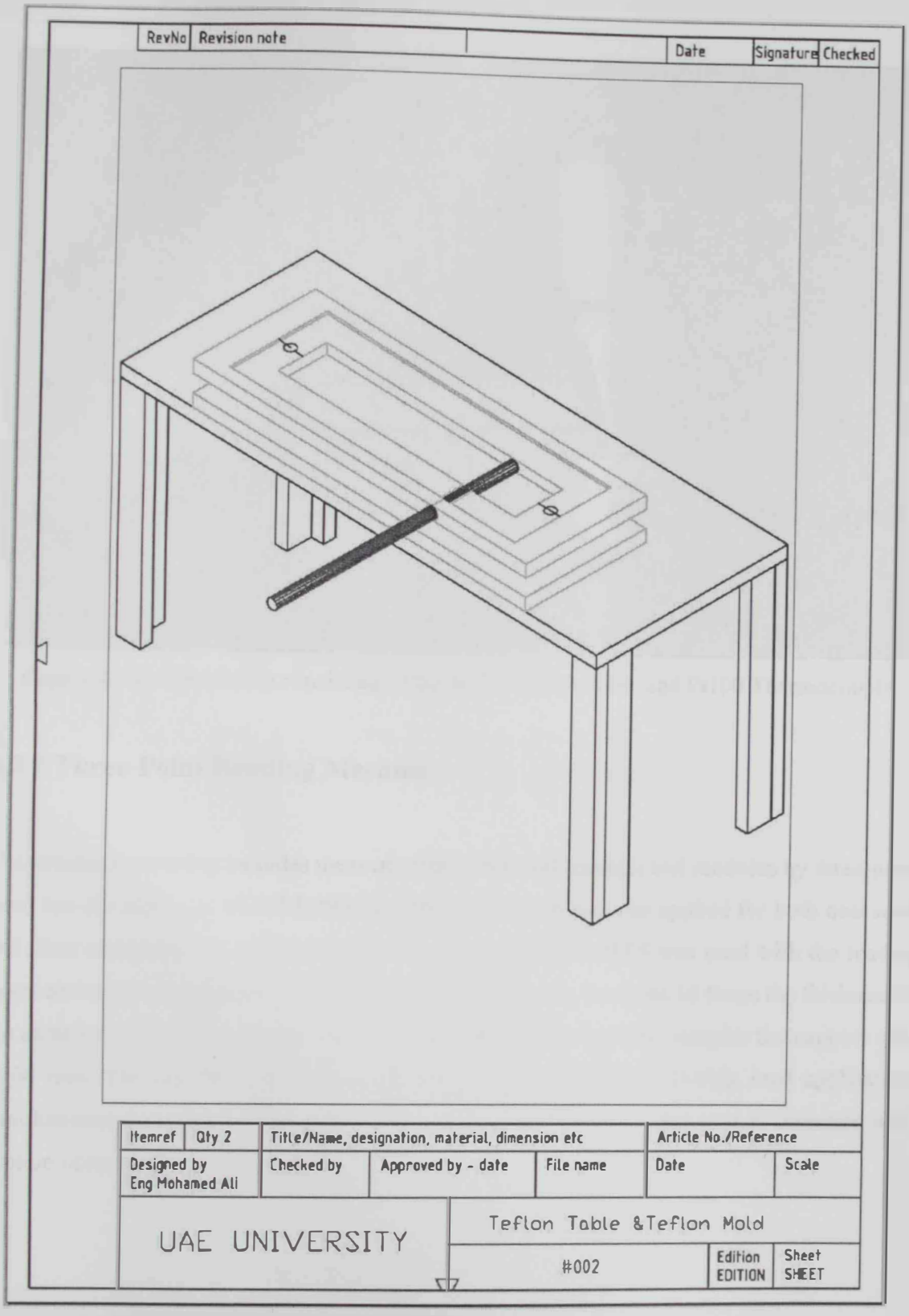

Figure 4.12: 3D modeling of the Teflon Table, mold, and thermocouple

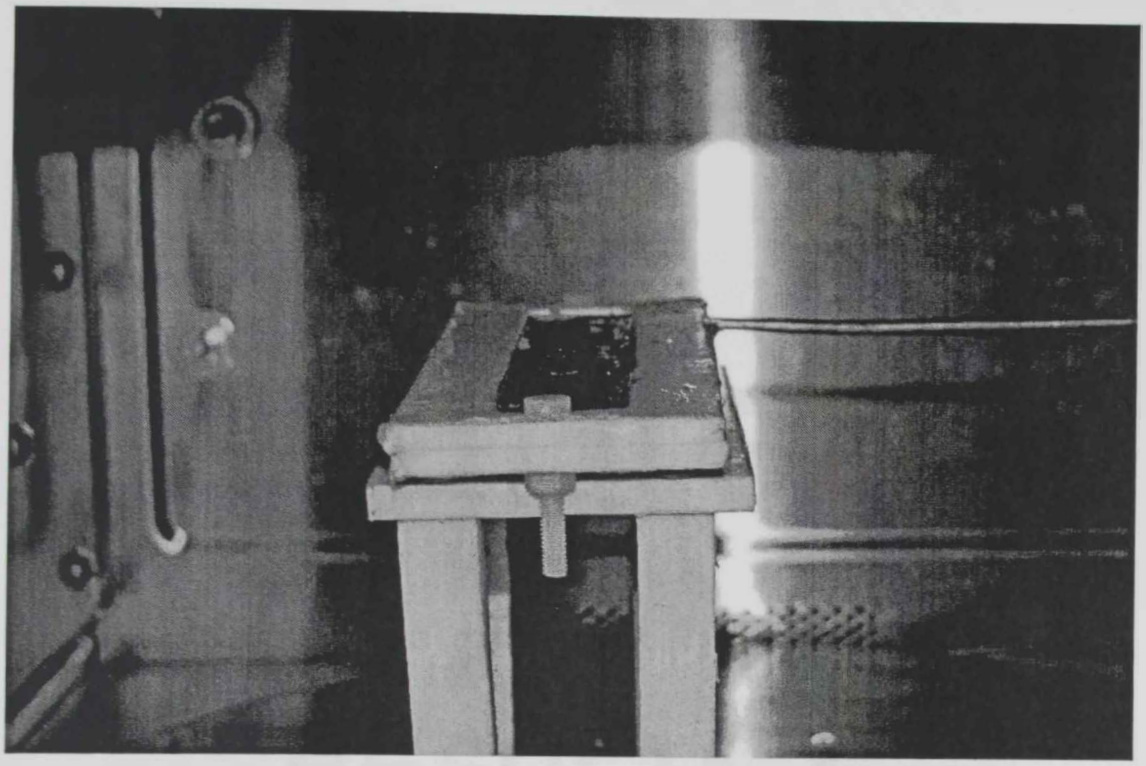

Figure 4.13: Mold Setup consisting of the mold, Teflon table, and Pt100 Thermocouple

4.3.2 Three-Point Bending Machine

The mechanical testing includes measurement of flexural strength and modulus by three-point bend test according to ASTM D790-02 (2003). This standard was applied for both neat resin and fiber composites. A calibrated material testing machine MTS was used with the loading noses and supports installed. The support span used for all tests was 16 times the thickness of the samples (tolerance ± 1). For the 4mm standard thickness of our samples the support span is 64 mm. The rate of crosshead motion used was 2.5 mm/min. During load application, simultaneous recording of load versus time was carried out. The specimen is deflected until rupture occurs in the outer surface.

Chapter 5

RESULTS & DISCUSSION

Chapter 5

Results & Discussion

5.1 Introduction

Our main objective as stated in chapter one is to maximize the mechanical properties of epoxy matrix composites and achieve minimum cycle time. It is an attempt to enrich our knowledge about the thermal, kinetic, and electromagnetic behavior during microwave heat delivery. Nevertheless, we need to assure a complete control over the process parameters and avoid undesired deviation from the curing path. Such deviations may lead to thermal runaways and material degredation. In this chapter we will present the experimental work of this thesis justified by data analysis. Before doing so we shall explain the logic behind the optimization approach. The first step was to carry out pretesting procedure to insitu investigate the cure behavior of epoxy resin. An isothermal kinetic model was fit and analyzed. In addition the pre testing work included efficiency calculation to estimate the expected heat losses of the microwave applicator. The second step was to design a cure cycle based on the pre testing data collected. Furthermore, both of the homogeneity of the cure and the mechanical properties of thermal and microwave curing were compared and analyzed. The effect of processing conditions such as gelation time, de-gassing, heating rate, and cure time has also been tested. Finally a conclusion was drawn to evaluate the results, compare them with reviewed literature, discuss the processing difficulties, and recommend future improvements.

5.2 Pre Testing

5.2.1 Cure Analysis of Epoxy Resin

During the curing process of this resin, complex chemical & thermal reactions take place. For a resin to achieve the ultimate physical & mechanical properties the nature of these reactions has to be studied and an optimized kinetic model has to be found for each type of resin. The kinetic model is also an effective way to facilitate numerical modeling of the polymerization process, study ageing and degradation mechanisms, and compare the behavior of resin with diverse forms of heat delivery. Differential Scanning Calorimetry (DSC) has been heavily utilized to find process parameters and estimate the thermal properties of polymers (Sundstorm et al, 1978; Cuadrado et al., 1983; Hsu et al., 1985; Oyanguren et al., 1993). In this particular research, the purpose of making DSC testing is to first provide heating profile for the calibration process of epoxy resin. More details will be mentioned in the microwave calibration section. Second purpose is to provide a reference point for optimization of the cure cycle of epoxy in microwave heating. A third purpose that we will find later in the future work section is to provide a working model for numerical modeling of the epoxy system. We will first introduce the methodology of cure detection and then explain the experimental procedure, the outcome, and data interpretations.

5.2.2 Kinetic Modeling

Two main kinetic parameters, degree of cure (α) and the rate of cure ($d\alpha/dt$) are measured by DSC. Degree of cure is generally defined as the partial exothermic or total heat generated at time t with respect to the total heat of reaction. In other words, degree of cure represents the maximum extent to which the cross link reaction has reached during polymerization. It is mathematically represented as (Sourour, 1978):

$$\alpha = \frac{\Delta H_t}{\Delta H} \qquad (5.1)$$

Where ΔH_t is the total heat generated at time t and ΔH is the ultimate heat obtained by dynamically scanning the material.

The rate of cure (da/dt) is measured based on the assumption that for a cure process, the measured heat flow (dH/dt) is proportional to the conversion rate (Boey & Qiang, 2000). Although this assumption is valid for single reaction with no other events such as evaporation of solvents or changes in heat capacity, it has been proven to be experimentally valid and reasonably accurate. Thus the following mathematical form can be used:

$$\frac{d\alpha}{dt} = \frac{dH / dt}{\Delta H} \qquad (5.2)$$

Both of dH/dt and ΔH can be obtained directly from the DSC thermogram. The basic two approaches are isothermal and dynamic scans. While isothermal scans monitor the polymerization process at a fixed temperature and thus at a fixed value of activation energy, the non-isothermal or dynamic scans continuously increase the temperature in a uniform rate. For our particular study, we shall use the isothermal study since it has the advantage of reducing the process variables and thus simplifying the modeling approach. Later in the experimental section we shall also utilize the isothermal curing method.

The function now of the kinetic model is to find a relationship between the experimentally obtained degree of cure and the rate of cure taking into consideration the activation energy of the process and the decrease in the amounts of functional groups as conversion progresses.

The curing models have been a vital area of development and many researchers have contributed in this field by suggesting kinetic models that vary extensively in applicability, simplicity, and accuracy. More details on different types of models and the use of each category are discussed elsewhere (Ali & Hammami, 2005). For our analysis we shall use an autocatalytic model which assumes that the step reaction products are involved in the chain growth reaction of the polymer. The mathematical representation of this model takes the following form (Kamal & Sourour, 1974):

$$\frac{d\alpha}{dt} = K(T)\alpha^m(1-\alpha)^n \qquad (5.3)$$

Where m and n are the reaction orders and K(T) is a temperature-dependant reaction rate constant that has an Arrhenius form:

$$K(T) = A\exp\left(-\frac{E_a}{RT}\right) \qquad (5.4)$$

Where A is a pre-exponential factor and E_a is the activation energy. Using the information detected from DSC we will obtain all the kinetic model parameters explained above.

The isoconversion method (Friedman, 1964) is utilized to linearize the relationship between the rate of cure and the degree of cure in equation 5.3. This method states that the reaction rate at constant degree of cure is a linear function of temperature only. The natural logarithm of the experimental rate of cure is taken:

$$\ln\frac{d\alpha}{dt} = \ln K(T) + m\ln\alpha + n\ln(1-\alpha)$$

$$\Rightarrow \ln\frac{d\alpha}{dt} = cons\tan t + m\ln\alpha + n\ln(1-\alpha) \qquad (5.5)$$

For each isothermal Temperature *K(T)* becomes a constant as shown in the previous equation. Non linear least square method which minimizes the square of the error between the predicted and the experimental data is widely used for the estimation of kinetic parameters due to simplicity and reasonable accuracy. Several other methods are also mentioned in the literature for parameter estimations. Box-Kanemasu method (Scott et al, 1993), graphical analytical method (Kenny, 1994), Runge Kutta method, (Lee et al., 2000) and several other methods proposed by Keenan (1987) and Ryan & Dutta (1979). For our analysis, we have chosen the more widely used least square method. The details of this method are mentioned elsewhere (Singiresu, 2001).

By fixing the value of α and letting *K(T)* as a variable, the previous equation can be rewritten as:

$$\ln\frac{d\alpha}{dt} = \ln A + \ln[\alpha^m(1-\alpha)^n] - \frac{E_a}{RT}$$

$$\Rightarrow \ln\frac{d\alpha}{dt} = cons\tan t - \frac{E_a}{RT} \qquad (5.6)$$

From this equation the slope of logarithmic rate of cure versus the reciprocal of the temperature leads to the activation energy divided by the gas constant. Although the model can be adequately described by the m, n, and K(T), calculation of the activation energy will strengthen the accuracy of the model and provide a means of detecting the kinetic changes through the reaction as will be shown later in the results section.

5.2.1.2 Kinetic Testing & Data Analysis

Since conditions of tests, specimens, and calibration of DSC equipment deeply affect the DSC heating curves and thus the cure kinetics, ISO standard 11357-5 (1999) is utilized to determine appropriate sample weights, scanning heating rates, thermal stability, and curve analysis. The ISO11357 series in fact includes data on many areas such as measurement of glass transition temperature, specific heat capacity, conversion kinetics, crystallization kinetics, and water adsorption. The standard will effectively unify the testing procedure and thus comparable data can be produced. Therefore, we strongly recommend the use of this standard for future work.

To prepare the mixture, the resin and curing agent were stirred homogenously for 10 minutes. The total amount of resin prepared was 30 grams to assure uniformity of mixture. Samples of 15-25 mg are then filled to the aluminum pans and placed in the DSC sample cell one by one. Weights, before and after analysis were measured to make sure no loss in weight. After each sample preparation, the excess resin was kept at about -10 °C to seize any pre-experimentation curing. For verification, a scanning thermogravimetric test (TGA) analysis is also carried out to monitor any possible loss in weight at the isothermal temperature [Figure

5.1]. Since the maximum isothermal temperature to be tested is 120 °C, the maximum weight loss is 1.5%, mainly minor solvent evaporation.

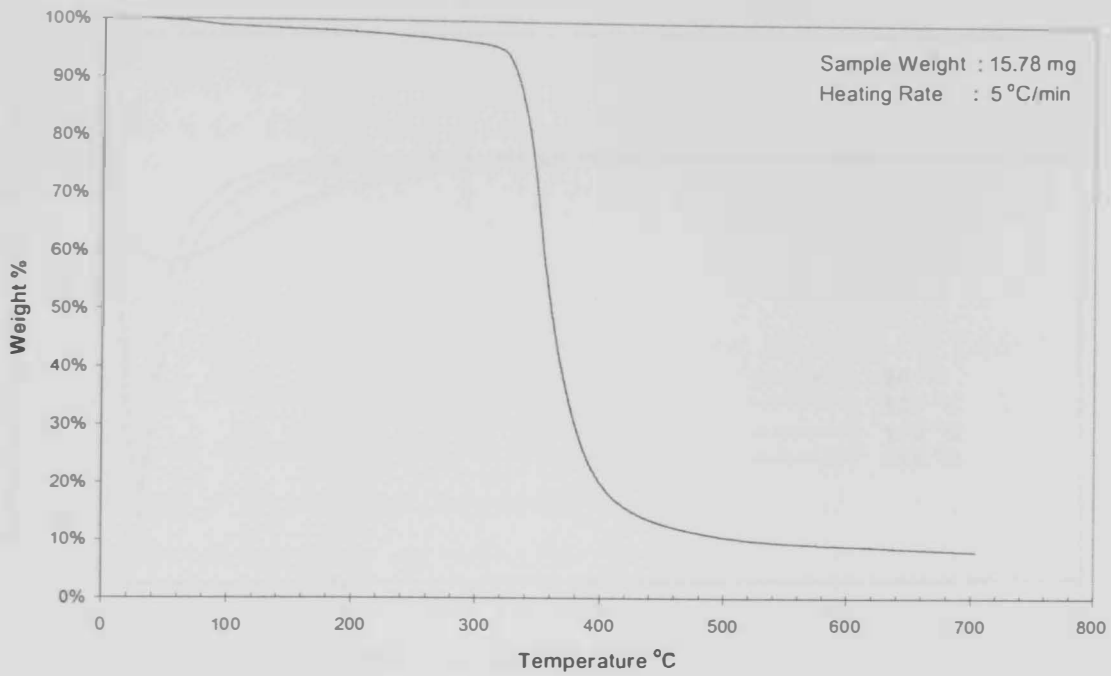

Figure 5.1: Thermogravimetric Analysis of DER324 Epoxy Resin

Isothermal runs were performed at four temperatures, 90 °C, 100 °C, 110 °C, and 120 °C. For each temperature, the sample was placed at the heating cell until base stability and then heated at a rate of 200 °C/min to the specified isothermal temperature. The high heating rate is used to minimize the amount of undetected heat due to system instability during heating. After that a 20 minutes stage dwelling is maintained to assure complete reaction. After testing, the sample was cooled back to room temperature and the experiment was repeated again to record the characteristic heating curve of the material without the exothermic reaction. The second curve is subtracted from the previous one to separate the exothermic reactions from heating data.

Figure 5.2 shows the normalized isothermal heat flow measured by DSC for the four curing temperatures of study. Normalization is important to cancel out the effect of mass variation on the specimen cure behavior. The isothermal conversion at isothermal cure of 90 °C, 100 °C, 110 °C, and 120 °C was completed after 21.8, 13.1, 8.9, and 4.4 minutes, respectively. We can immediately notice the increase in the rate of the polymerization reaction as the isothermal temperature increases. In addition, when dealing with microwave curing the DSC curing time

will provide the starting point for cycle optimization and provide rich data for analysis and comparison.

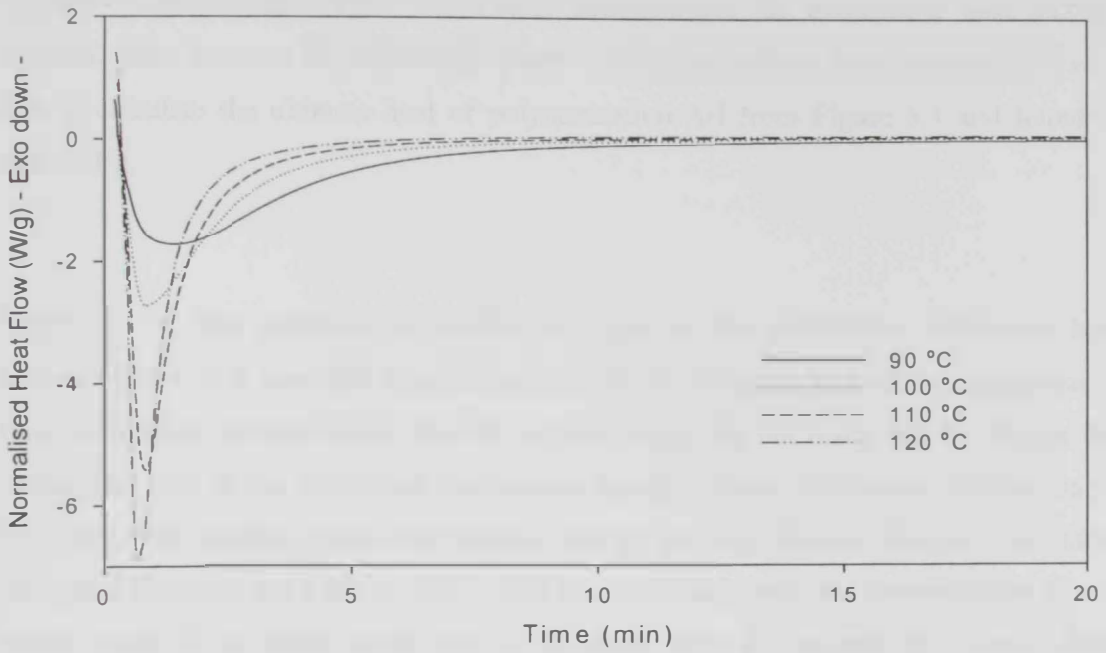

Figure 5.2: Normalized Isothermal Heat Flow at 90, 100, 110, and 120 °C

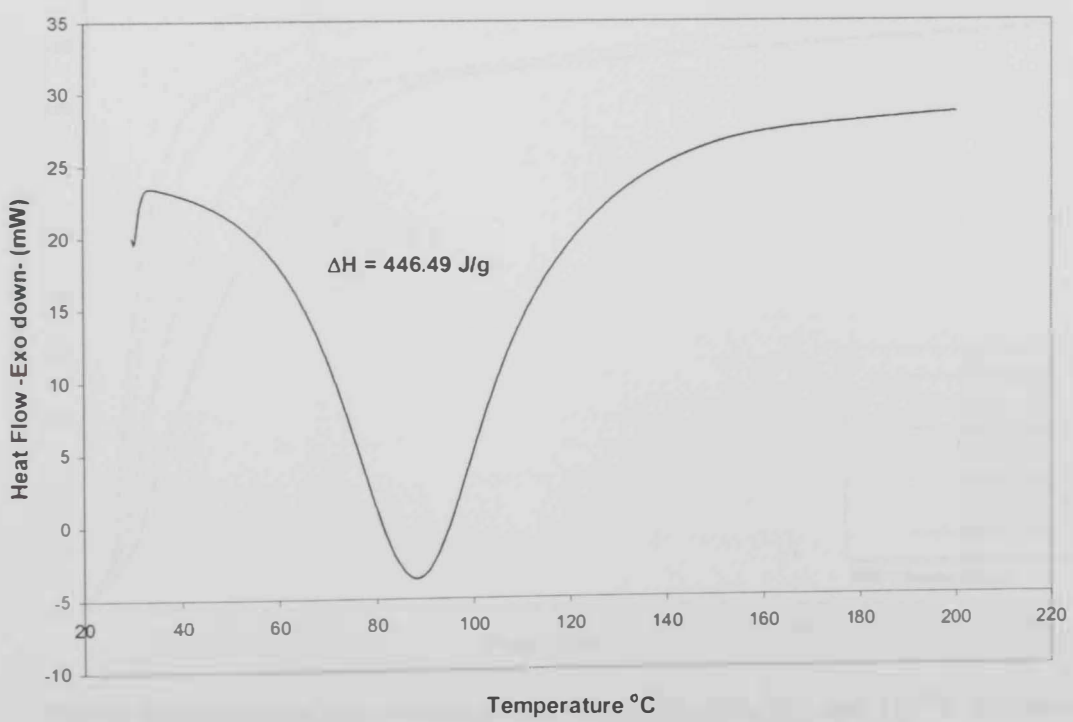

Figure 5.3: Heat Flow of Dynamic DSC scan at 5 °C/min

On the other hand, a dynamic scan is also carried out from 30 °C to 200 °C at a rate of 5 °C/min in order to obtain the ultimate heat of polymerization ΔH in equation 5.1. This heat of polymerization is usually obtained by dynamic scan to avoid any minor heat loss during isothermal ramp stage. Figure 5.3 clearly demonstrates the exothermic heat during the dynamic scan. In order to measure the degree of cure as defined from equation 5.1, we first had to calculate the ultimate heat of polymerization ΔH from Figure 5.3 and found to be 446.49 J/g.

Figure 5.4 is then produced by finding the ratio of the progressive isothermal heat of polymerization at a specified temperature, ΔH_t to the ultimate heat of polymerization, ΔH. From this figure we can notice that the degree of cure did not reach 100 %. This is due to incomplete cure at the isothermal temperature resulting from vitrification. At this stage the mobility of the reacting groups are hindered and the cure mechanism changes to be diffusion controlled (Yousefi and Lafleur, 1997). The low scanning rate in the dynamic scan, however, detects most of the minor heats even at diffusion stage to represent the ultimate heat of polymerization.

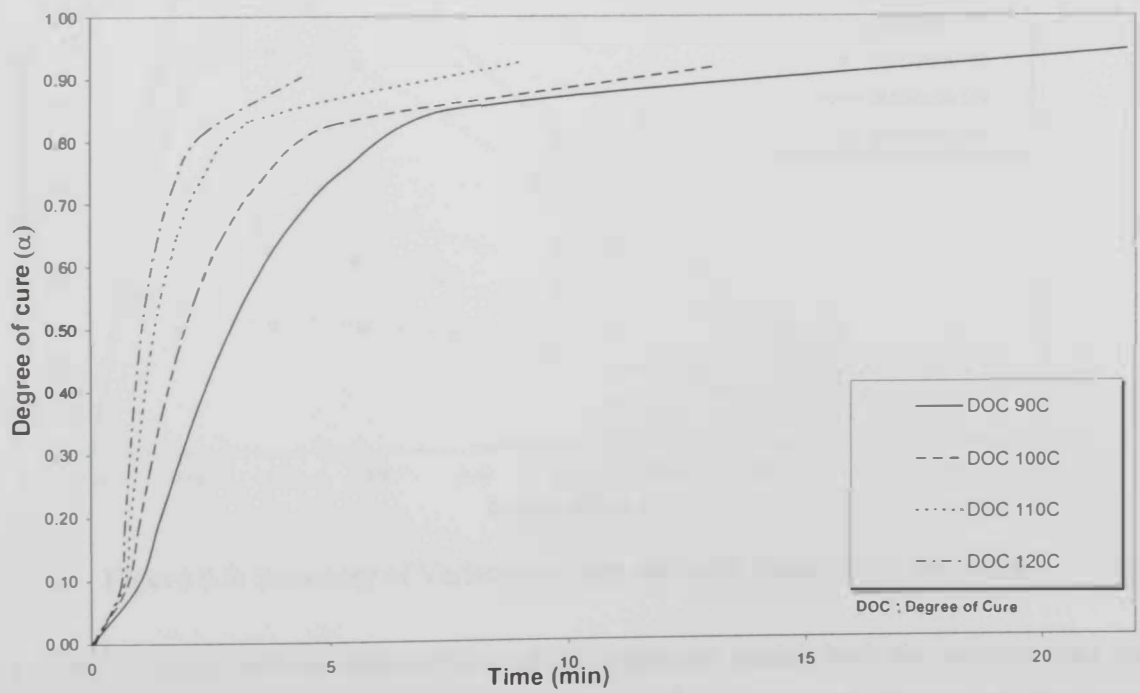

Figure 5.4: Degree of cure variation with time at 90, 100, 110, and 120 °C Isothermal Temperature

Since the derivative data $d\alpha/dt$ is also generated automatically from DSC tests, the experimental values of α and $d\alpha/dt$ are then processed using the least square method to determine the model parameters of equation 5.5, namely m, n, and *K(T)*. Table 5.1 states the calculated isothermal parameters. The average (m + n) value is 2.28 which agree with values obtained with other epoxy formulations (Malek, 1992).

Table 5.1: Estimation of Isothermal Kinetic Model

Temp °C	ΔH (J/g)	Kinetics Parameters				
		m	n	K	A	Ea (KJ/gm)
90	422.15	0.41	1.60	0.83	2.37E+07	51.8
100	410	0.37	1.77	1.27	2.28E+07	
110	413.69	0.48	2.01	3.10	3.59E+07	
120	403.5	0.45	2.02	3.78	2.90E+07	
Mean		0.43	1.85	2.25	2.79E+07	51.8

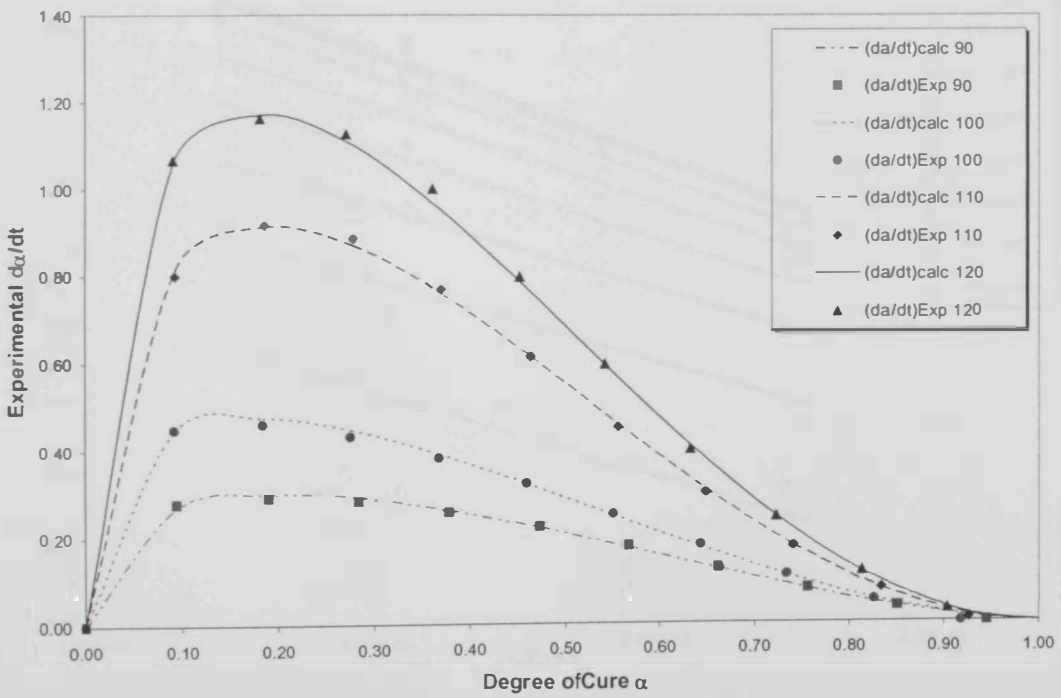

Figure 5.5: Summary of Variation of cure rate with respect to degree of cure

In order to appreciate the compatibility of the empirical model, both the experimental and calculated rates of cure are plotted for each isothermal temperature in Figure 5.5. The figure shows good correlation between the calculated and the experimental data with the maximum

rate of cure obtained at about $\alpha = 0.2$, which agrees with the mathematical characteristic of the autocatalytic model of equation 5.3. The maximum observed error in the rate of cure between the experimental and modeled data was found to be 4% at 100 °C. Yet, the maximum error values declines at the rest of the curves to reach 2 %.

The average calculated activation energy is also indicated in Table 5.1. The value was found to be 51.8 ± 6 KJ/mol. This value was obtained from Figure 5.6 by measuring the slope of the straight line fit of the data as shown in equation 5.6. The average activation energy agrees with the values obtained for similar epoxy-amine formulations. According to Malek (1992), the observed values of activation energy was 58 KJ/mol. Montserrat et al. (2003) obtained an average value of E_a = 57.9 ± 4.4 KJ/mol. Montserrat also quoted in his work that Vercher (1990) obtained values of E_a between 56 & 59 KJ/mol.

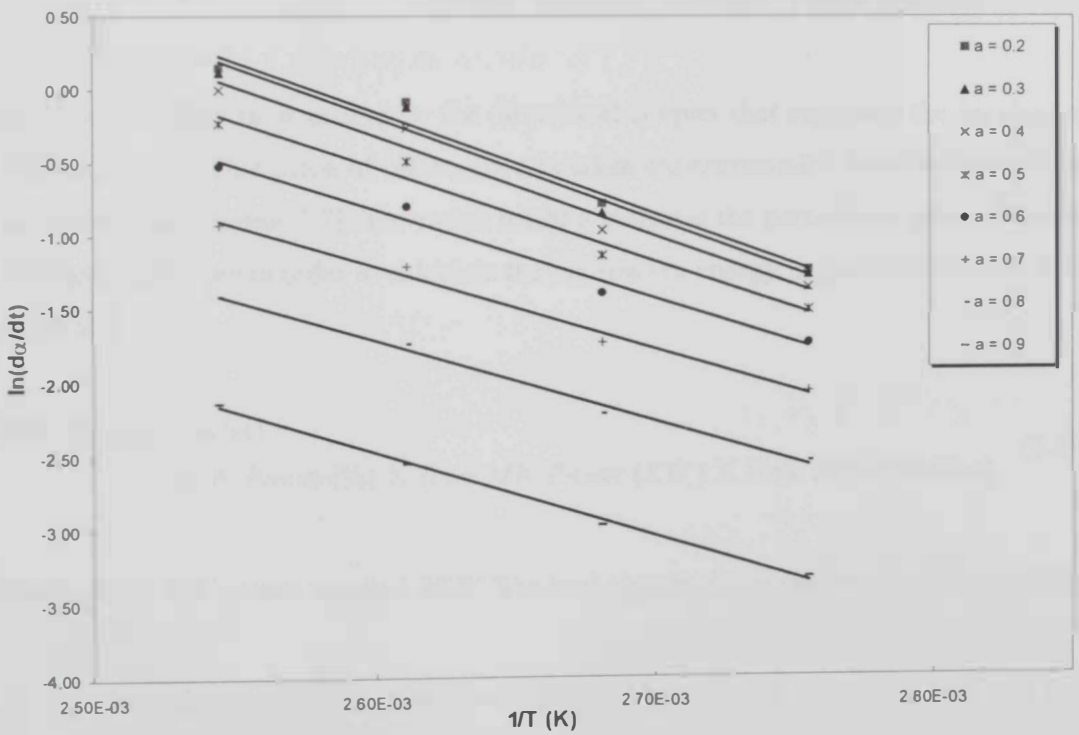

Figure 5.6: Linearization of rate of cure versus the temperature reciprocal

5.2.2 System Calibration

After accurately describing the isothermal behavior of epoxy resin during cure, we will start calibrating the microwave energy consumption and study whether DSC could assist in getting reliable data. In system calibration we would like to approximate heat losses in the heating process of microwave samples. This is essential to read all the power absorption curves to be later generated in the experimental work. According to Fricke & Mallah Company, manufacturer of the system, the heat losses is about 20 %. They are mainly represented in heat absorbed by cavity walls and waveguides. The measurement is based on the basic energy conservation concept:

$$[MW\ Energy\ Delivered - MW\ Energy\ \mathrm{Re}jected] = [Heat\ Absorbed\ by\ Sample + Heat\ Losses] \tag{5.7}$$

Microwave energy is measured by the directional coupler that separates the incident and the reflected waves. This piece of information is taken experimentally from the power meters in the control unit [Figure 5.7]. The meter reading indicates the percentage power delivered and reflected. Therefore in order to calculate the microwave energy in joules we use the following equation:

$$MW\ Energy\ (Joules) = MW\ Power\ (\%)\ X\ Total\ MW\ Power\ (KW)\ X\ Time\ Duration\ (Sec) \tag{5.8}$$

Where Total MW power equals 1.9KW.The heat absorbed can also be approximated by:

$$Heat\ Absorbed\ by\ Sample(J) = m(g)\ C_p(J/g.^\circ C)\ \Delta T(^\circ C) \tag{5.9}$$

Where m is the mass of the sample, C_p is the specific heat of the material, and ΔT is the temperature difference before and after microwave heating. Two materials were chosen to measure the efficiency. First water samples are tested. Water has the advantage of quick reaction to microwave energy and well known dielectric properties. Usually it is the first choice in any calibration process to obtain rapid and reliable data. Second material is the

material under investigation, epoxy resin. In the coming two sections we will show the measured data and the calculations sheet in addition to the heating charts.

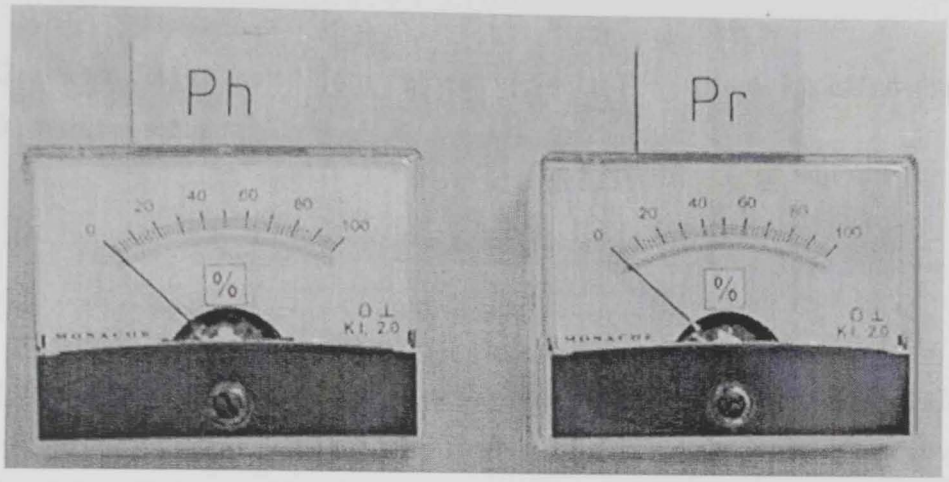

Figure 5.7: Incident & Reflected Power Meters.

5.2.2.1 Efficiency Calculation of Water

Four samples of water were weighed and placed in polystyrene cups. The shielded thermocouple is inserted inside the cups for temperature measurement.

Table 5.2: Calculation Sheet of Water Calibration Samples

Sample	No#1	No#2	No#3	No#4
Cup Weight (gm)	2.83	2.83	2.83	2.85
Total Weight (gm)	168.61	168.61	168.61	168.61
Water Weight (gm)	165.78	165.78	165.78	165.78
Power Level %	20	20	20	20
Reflected Power %	6	6	6	6
T1 (°C)	26.15	22.92	19.46	22.84
T2 (°C)	71.92	77.67	75.54	75.04
Heating duration (sec)	156	181	179	172
Net MW Energy Delivered (J)	41,496.0	48,146.0	47,614.0	45,752.0
Heat Absorbed (J)	31,792.7	38,030.3	38,954.2	36,259.1
Efficiency %	**76.6**	**79.0**	**81.8**	**79.3**

Different time durations were applied for each one of the samples to increase the reliability of the calculations and to obtain time-independent efficiency. Incident power rating of 20% was

fixed in all the samples. Figures 5.8 to 5.11 present the variation in temperature during the 20% power cycle. We can notice that the rate of increase in temperature is constant indicating no change in specific heat of the system and thus the reliability of the data.

Table 5.2 lists the data collected from the heating charts. The efficiency is calculated for each sample from this equation:

$$Heating\ Efficiency = \frac{Net\ Heat\ Absorbed}{Net\ MW\ Energy\ Delivered} \qquad (5.10)$$

Net heat absorbed is calculated from equation 5.9 while the net MW energy delivered is calculated from equation 5.8. The last three rows in table 5.2 show the net heat delivered and absorbed and the efficiency of heating. Specific Heat C_p for water is taken to be 4.19 J/g.°C. Table 5.2 indicates that the heating efficiency ranges between 76.6% and 81.8% with an average of 79.2%. The experimental data is therefore very close to the 80% efficiency achieved by manufacturer. The remaining are losses due to heat absorbed by walls and waveguide, heat convection, and minor water evaporation. To minimize the last error the temperature is kept far below water boiling temperature. It is worthwhile mentioning that the aim of calibration is to obtain a fairly accurate sense of the system and to avoid any major energy losses.

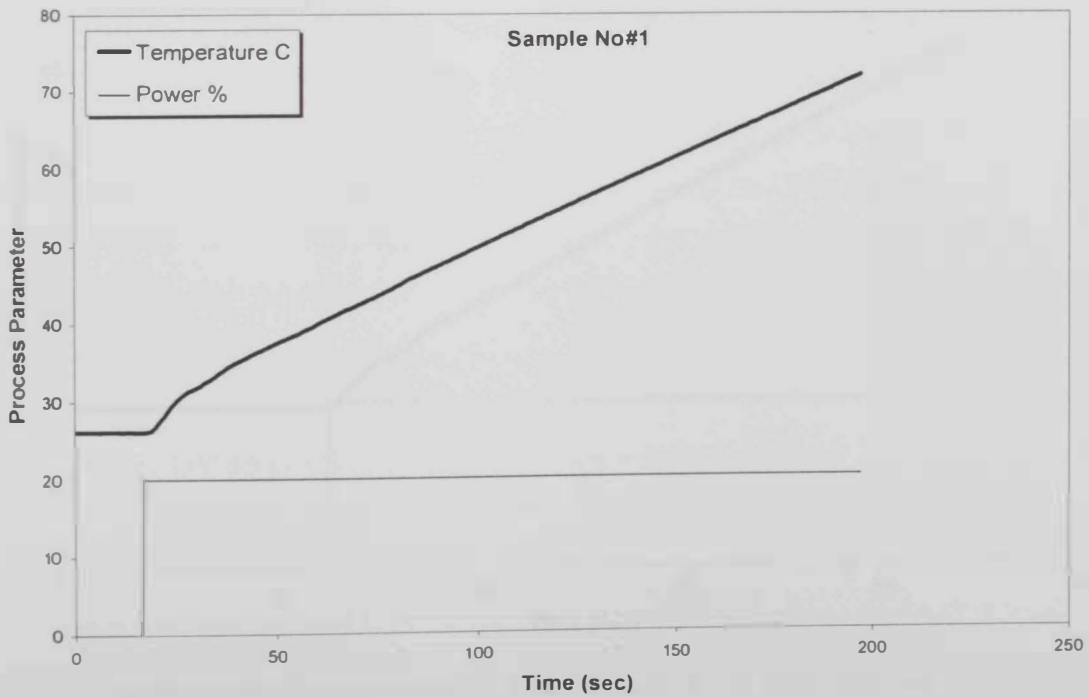

Figure 5.8: Heating curve of Water Sample # 1 at 20% power of 1.9 KW

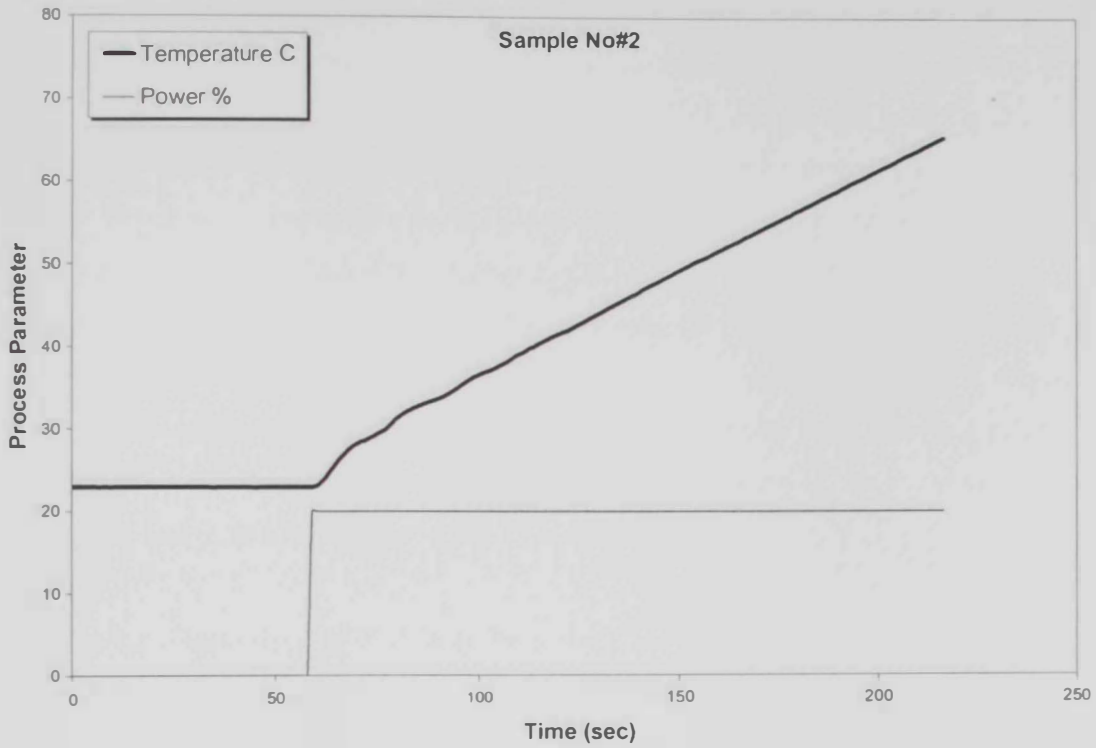

Figure 5.9: Heating curve of Water Sample # 2 at 20% power of 1.9 KW

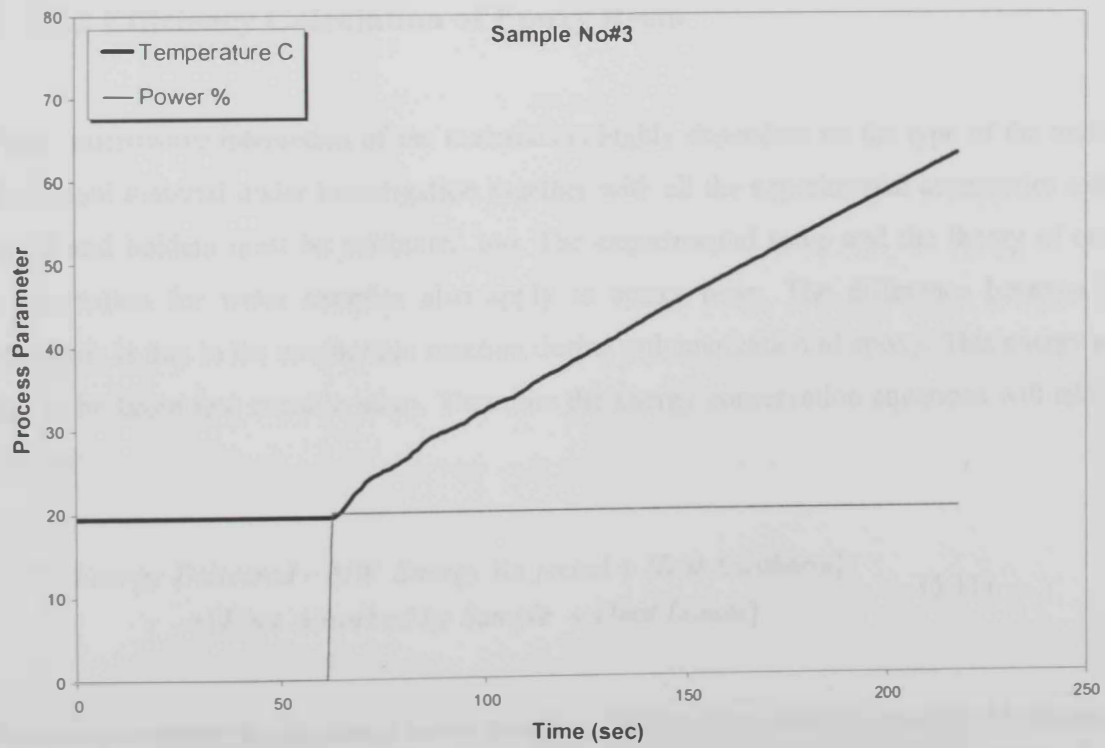

Figure 5.10: Heating curve of Water Sample # 3 at 20% power of 1.9 KW

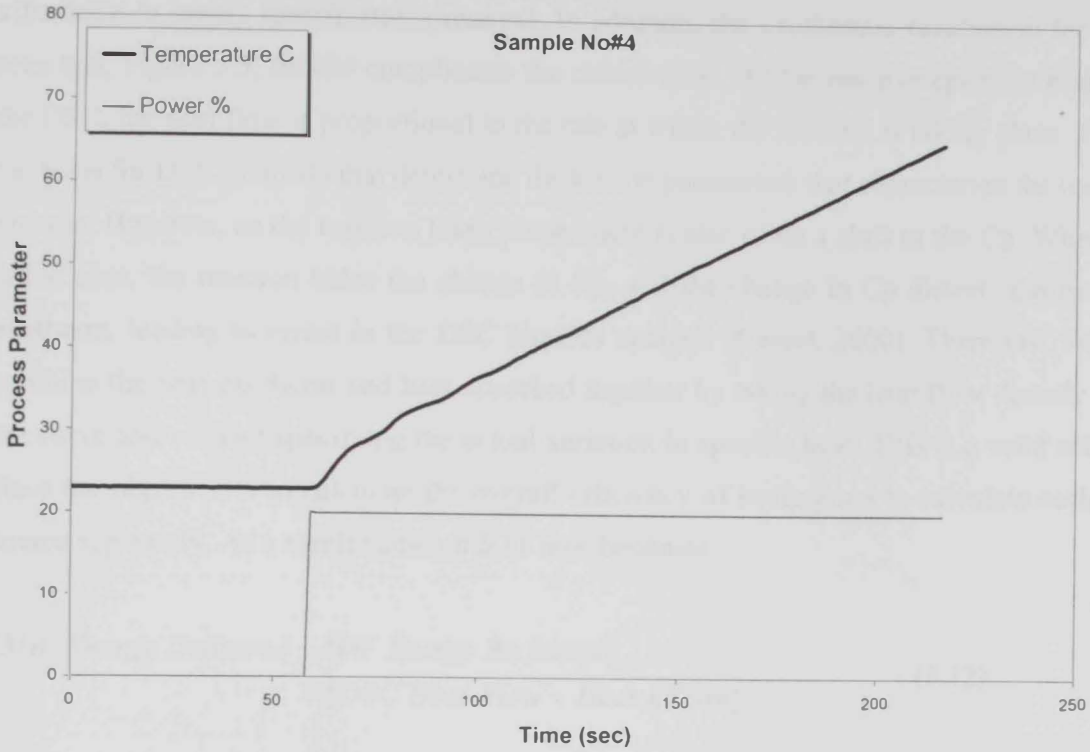

Figure 5.11: Heating curve of Water Sample # 4 at 20% power of 1.9 KW

5.2.2.2 Efficiency Calculation of Epoxy Resin

Since microwave interaction of the materials is highly dependent on the type of the material, the actual material under investigation together with all the experimental accessories such as mold and holders must be calibrated too. The experimental setup and the theory of energy conservation for water samples also apply to epoxy resin. The difference between both materials is due to the exothermic reaction during polymerization of epoxy. This energy input has to be taken into consideration. Therefore the energy conservation equations will take this format:

$$[MW\ Energy\ Delivered - MW\ Energy\ \text{Re}jected + Heat\ Exotherm] = [Heat\ Absorbed\ by\ Sample + Heat\ Losses] \quad (5.11)$$

Microwave energy is calculated using equation 5.8. On the contrary, equation 5.9 can not be used to calculate the heat absorbed by the resin since the specific heat of epoxy is a

temperature dependant variable and can not be assumed to be constant. Such data are not affordable in epoxy specifications manual. In addition, the exothermic reaction in the DSC scan test, Figure 5.3, further complicates the calculations. As the reactive epoxy is heated in the DSC, the heat flow is proportional to the rate at which the reaction is taking place. This is the basis for DSC methods that determine the kinetic parameters that characterize the reaction process. However, as the reaction takes place, there is also often a shift in the Cp. When this is the case, the reaction hides the change in Cp, and the change in Cp distorts the reaction exotherm, leading to errors in the DSC kinetics analysis (Cassel, 2000). Therefore, we will combine the heat exotherm and heat absorbed together by taking the heat flow directly from the curve and without specifying the actual variation in specific heat. This is a valid solution since the objective is to calculate the overall efficiency of heating not to calculate each heat source separately. As a result equation 5.11 now becomes:

$$[MW\ Energy\ Delivered - MW\ Energy\ \mathrm{Re}jected] = [DSC\ Heat\ Flow + Heat\ Losses] \tag{5.12}$$

Based on this final equation, Table 5.3 shows the results of heating 4 epoxy samples of epoxy. We have reduced the active heat duration to 100 seconds only to avoid the major "kick off" of the exothermic reaction and reduce the experimental error. Therefore, although Figure 5.12 to Figure 5.16 shows that the cure cycle is far beyond the 100 second duration, the studied duration is 100 seconds only as shown in Table 5.3.

The efficiency value ranged between 50 % and 70 %. The average value is about 62% which is less than the efficiency of water but yet still comparable to manufacturer recommendation. This is expected due to first water being an ideal dielectric material and excellent microwave absorber. Second, the exothermic reaction in epoxy reaction is approximated from DSC testing which is basically a thermal heating method. Huge debate has been raised on whether the microwave curing reaction has the same nature as the thermal one. This debate has been fully described in the literature review chapter.

Table 5.3: Calculation Sheet of Epoxy Calibration Samples

Sample No	1	2	3	4
Resin Wt (g)	28.18	20.97	23.74	35.25
Curing agent Wt (g)	2.95	2.21	2.49	3.7
Epoxy Wt (g)	49.1	47.89	46.8	45
Power Level %	20	20	20	20
Reflected Power %	11	11	11	11
T1 (°C)	33.84	32.48	32.48	33.24
T2 (°C)	54.8	56.2	61.6	70
Duration (sec)	100.0	100.0	100.0	100.0
Microwave Input Heat (J)	17,100.0	17,100.0	17,100.0	17,100.0
Heat Absorbed (J)	9,263.8	9,493.6	10,871.6	12,312.8
Efficiency (%)	**54.2**	**55.5**	**63.6**	**72.0**

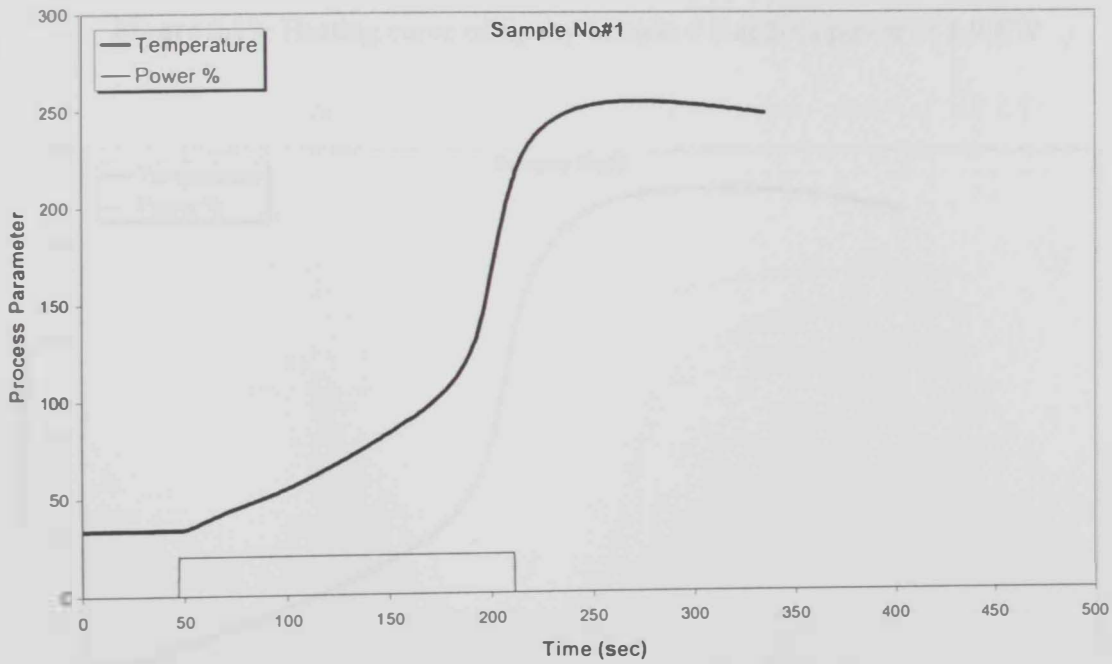

Figure 5.12: Heating curve of Epoxy Sample # 1 at 20% power of 1.9 KW

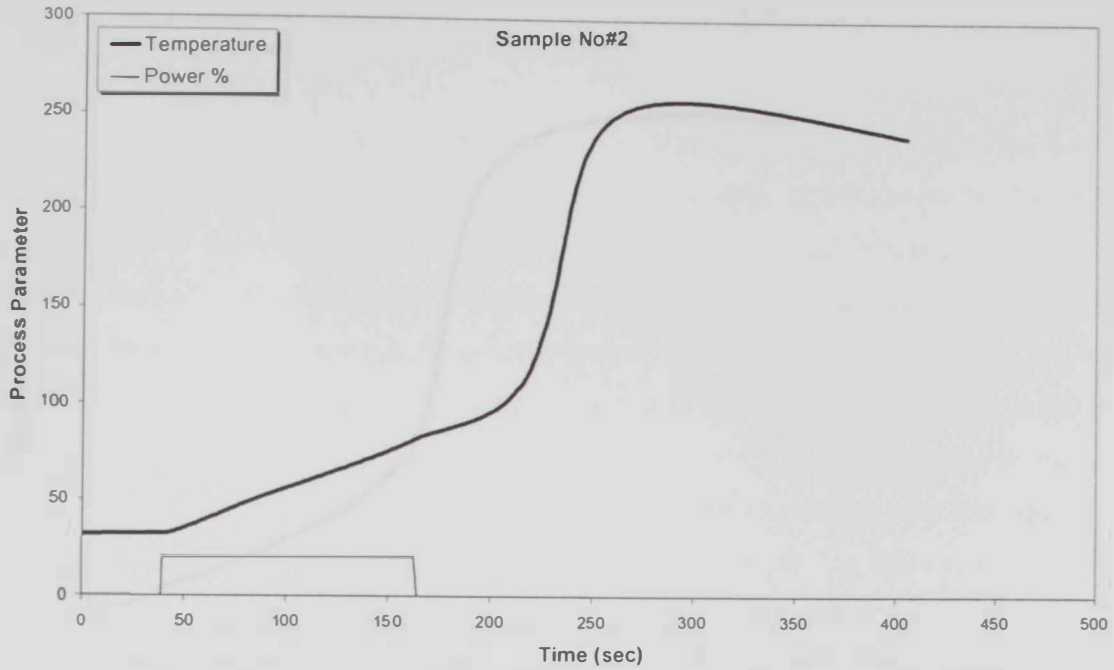

Figure 5.13: Heating curve of Epoxy Sample # 2 at 20% power of 1.9 KW

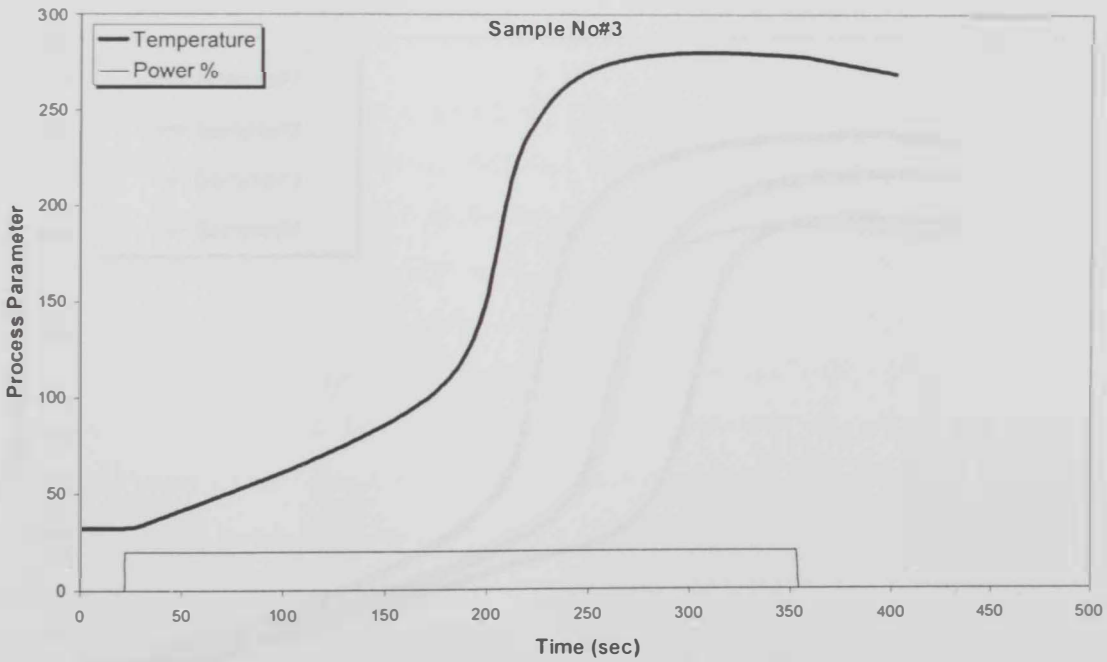

Figure 5.14: Heating curve of Epoxy Sample # 3 at 20% power of 1.9 KW

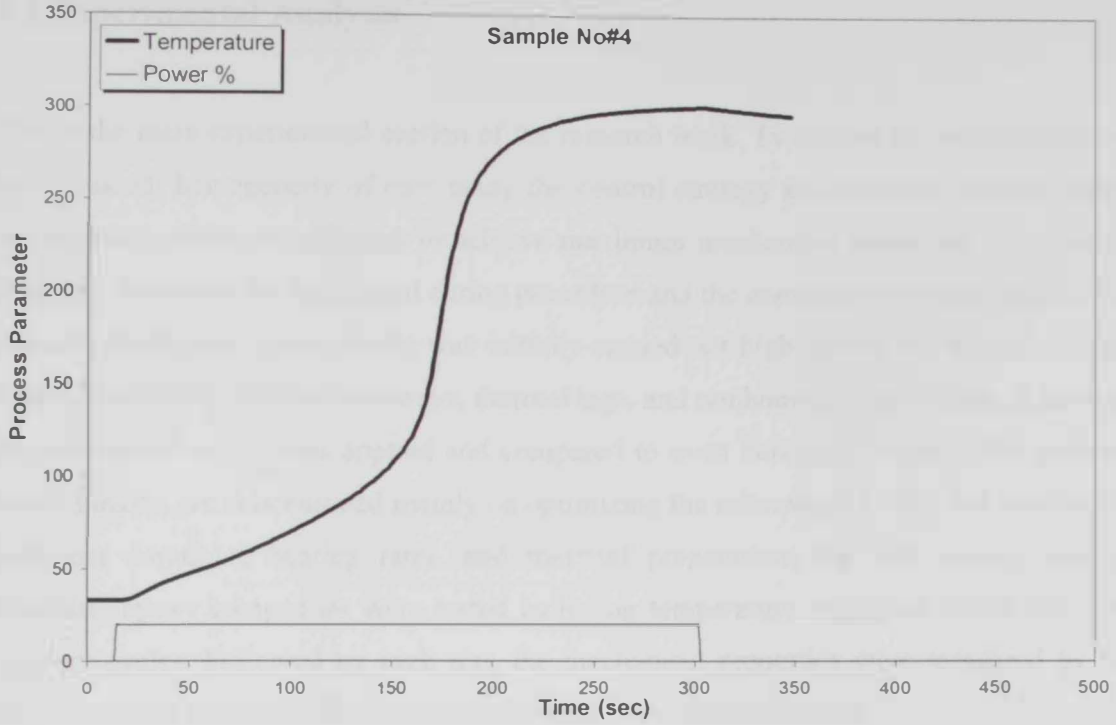

Figure 5.15: Heating curve of Epoxy Sample # 4 at 20% power of 1.9 KW

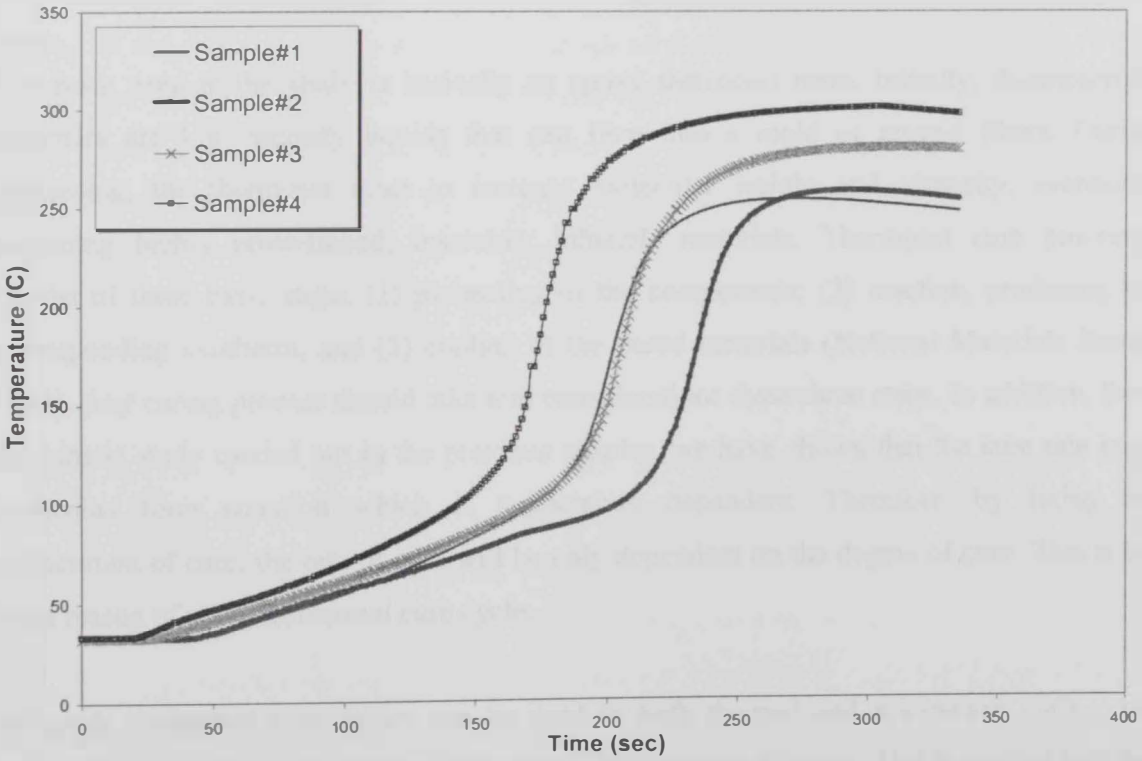

Figure 5.16: Summary of Microwave Heating of Epoxy Samples

5.3 Experimental Analysis

This is the main experimental section of the research work. Two areas of concentrations will be discussed, homogeneity of cure using the control strategy in microwave heating and the optimization of the cure process to achieve maximum mechanical properties. First, we will generally introduce the isothermal curing procedure and the associated variables such as ramp rate and dwell time. Oven curing was initially carried out highlighting the major processing drawbacks such as thermal runaways, thermal lags, and nonhomogeneity of cure. Afterwards, the microwave curing was applied and compared to oven curing for a particular isothermal cycle. Finally, we concentrated mainly on optimizing the microwave isothermal cure process. Different durations, heating rates, and material preparations for both epoxy resin and fiberglass/epoxy composites were tested including temperature variations charts and power delivery cycles. Followed by each test, the mechanical properties were measured by four-point bend test so that the best testing conditions could be highlighted.

5.3.1 Design of Curing Cycle

The resin used in the study is basically an epoxy thermoset resin. Initially, thermosetting polymers are low-viscosity liquids that can flow into a mold or around fibers. During processing, the thermoset react to increase molecular weight and viscosity, eventually becoming highly cross-linked, insoluble, infusible materials. Thermoset cure processes consist of three basic steps: (1) preheating of the components; (2) reaction, producing the corresponding exotherm; and (3) cooling of the cured materials (National Materials Board, 1994). Any curing process should take into considerations these three steps. In addition, from the kinetic study carried out in the previous chapter, we have shown that the cure rate is an Arrhenius form equation which is temperature dependant. Therefore, by fixing the temperature of cure, the rate of cure will be only dependent on the degree of cure. This is the main reason of using isothermal cure cycle.

Although isothermal cure cycles can be used in both thermal and microwave curing, the design of cure cycle under microwave heating is extensively different. This is due the fact that microwave can rapidly and volumetrically heat the material. In conventional curing cycle, the material has to be oftenly heated in stages to avoid sharp thermal gradient and excessive

heating of surfaces in addition to minimize the thermal lag between the oven and the part [Figure 5.17].

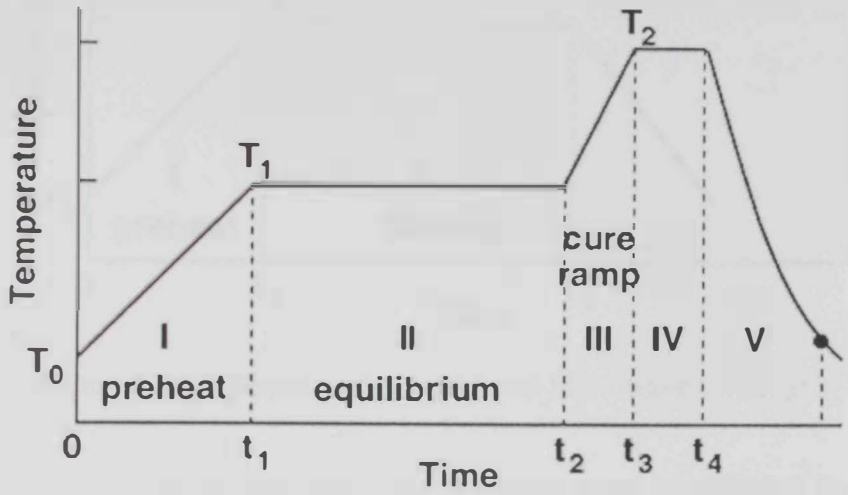

Figure 5.17: Schematic of a standard thermal Cure Cycle

The first stage is to heat the material to temperature T_1, where T_1 must be below the curing temperature at which the cross-linking starts. The temperature T_1 will be kept for the time t_2 so that all the resin is uniformly heated throughout the thickness of the composite. When thermal equilibrium is achieved, the temperature will be raised to temperature T_2, where the curing reaction starts. Afterwards, the temperature T_2 will be maintained until time t_4 assuring that the conversion is complete. In the final stage, the temperature is decreased to room temperature. It is worthwhile mentioning that the number of equilibrium stages will vary according to the thickness of the composite. The thicker the composite, the higher is the number of equilibrium stages.

Microwave curing cycle on the other hand is different as shown in Figure 5.18. There is no need for equilibrium steps to homogenize the temperature in the part due to volumetric heating characteristic of electromagnetic waves. This cure cycle holds for reasonably thick composites parts. If the penetration depth of electromagnetic field is less than the thickness of the material, modifications should be carried out. As was seen in equation 2.8 penetration depth is a function of frequency and dielectric properties.

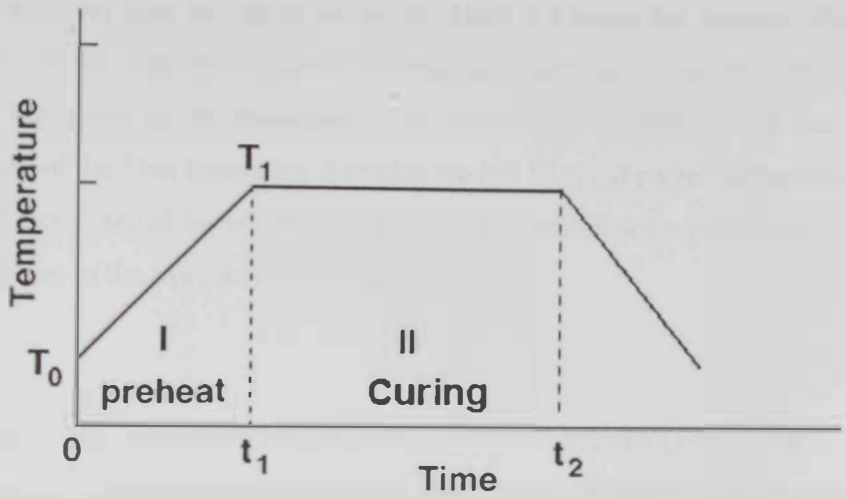

Figure 5.18: Schematic of an isothermal Microwave Cure Cycle

Despite the fact that conventional cure cycle is usually more complicated than microwave one, we have used single ramp, single dwell cycle for both conventional and microwave heating. The thickness of samples as described in Chapter 4 was 4 mm. Therefore thermal gradient is not large enough to require multiple-stage cycles.

5.3.2 Oven curing

In oven curing, different experimental activities have been carried out. Since our efforts are directed towards optimizing microwave curing cycle, oven curing cycle was used as a reference and thus a standard cure cycle, recommended by supplier, has been assigned for thermal curing. Table 5.4 reports the recommended cure cycle assigned by Dow Chemical Company for DEH20 curing agent. Since oven samples are small in both mass and size, 80X16X4 mm, the expected exotherm is also small and thus one hour dwelling was used rather than two hours. Regarding the ramp rate, this was left for the oven system facility. The oven control system allows only setting a target temperature without specifying a heating rate. Later, the heating rate was measured experimentally and found to be around 10 °C/min.

Sample preparation involves mixing the resin and the curing agent in paper cups according to stoichiometric ratio described in Chapter 4. Continuous stirring for 10 minutes are then applied to evenly distribute the curing agent. Additional 10 minutes are taken for air degassing. For neat resin samples, the Aluminum molds are filled using a plastic syringe. The fiberglass samples were molded using a lay-up technique. Each fiber layer is inserted into

mixed resin bath and then laid up in the mold. Table 5.5 states the number of layers in each mold and the volume fraction measured by burn test (ASTM D2584-02, 2002). The volume fraction was kept small due to processing difficulty as the small sample size does not facilitate simple packing of the fiber laminates. Samples are left to gel at room temperature, 45 minutes duration, and then inserted for one hour at 100 °C. Two samples are processed at a time due to the size limitation of the oven as seen in Figure 5.19.

Table 5.4: Cure cycle recommended by Dow Chemical Company (Dow, 1999)

Curing Agent	Suggested Cure Schedule	Source	Comments
DEH. 20	Gel at RT plus several days at RT or 1-2 hrs at 100°C for full cure	Dow Chemical Company	General purpose RT curing agent. High exotherm in large mass

Table 5.5: Epoxy/Glass Fiber Molding Details

Molding Method	Sample Size LXWXT (mm)	Laminates / Mold	Volume Fraction
Hand Lay-up	80X16X4	4	10%

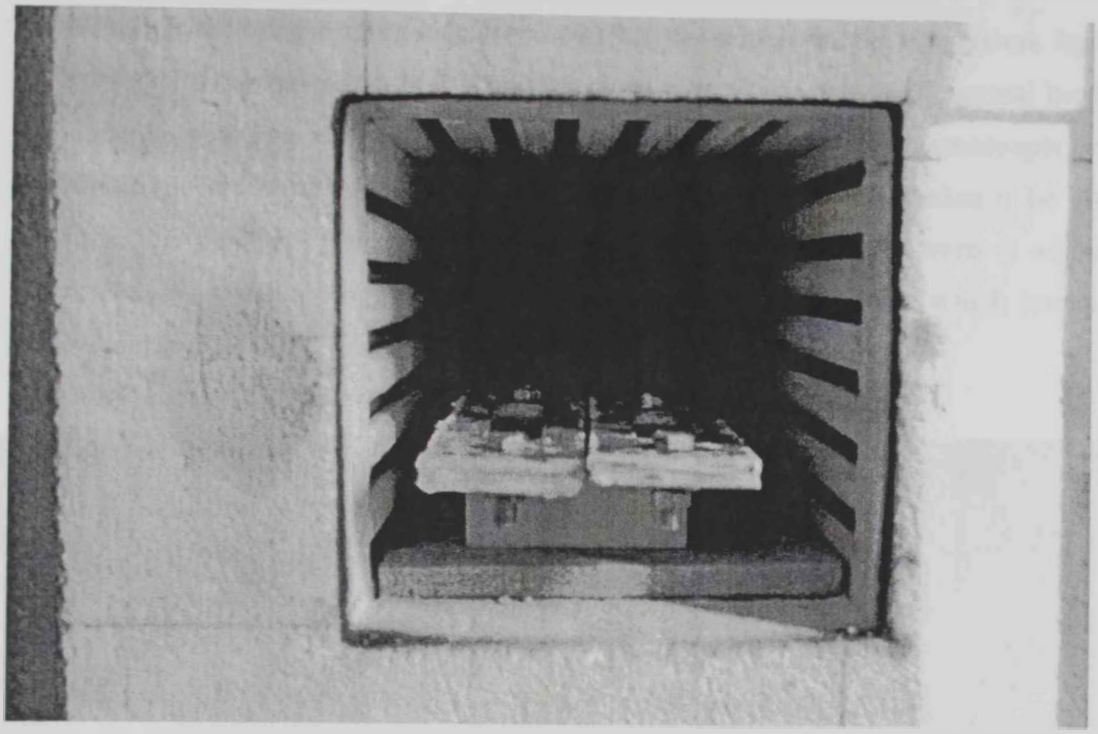

Figure 5.19: Two Samples Packing of Oven Cavity

Total of 15 successful samples were processed, five samples for neat resin, fiber glass reinforced composite, and carbon fiber reinforced composite. The carbon fibers were first taken as additional research material. However, processing difficulty for microwave heating prevented the full analysis of these fibers.

Two issues will be discussed in oven curing. The first one is homogeneity of cure and the second is mechanical properties which will be dealt with in separate section. Regarding the first issue, three thermocouples were used to measure the temperature of sample, mold, and cavity. The three thermocouples were attached to a data acquisition system controlled by Labview® program to store the data [Figure 5.20]. The aim is to detect the thermal gradient and the accuracy of the oven controller. Figure 5.21 shows the result of oven curing for neat resin. Isothermal cure cycle at 100 °C was selected. The dwell time is taken to be more than one hour. Since this cycle is for demonstration only, i.e. not for mechanical testing, the exact dwell time of one hour was not followed to allow for more time for thermal gradient measurement.

Several remarks can be observed from Figure 5.21:

A- Although the oven controller is set to 100 °C, the actual sample temperature further exceeded to be around 112 °C. This clearly shows the inaccuracy of thermal heating since the power adjustment is due to the temperature of the oven thermocouple only. This built-in thermocouple is located at the back of oven which makes it far away from the sample. Furthermore, the temperature controller of the oven is adjusted mechanically by rotating the gauge to the specified temperature which increases inaccuracy.

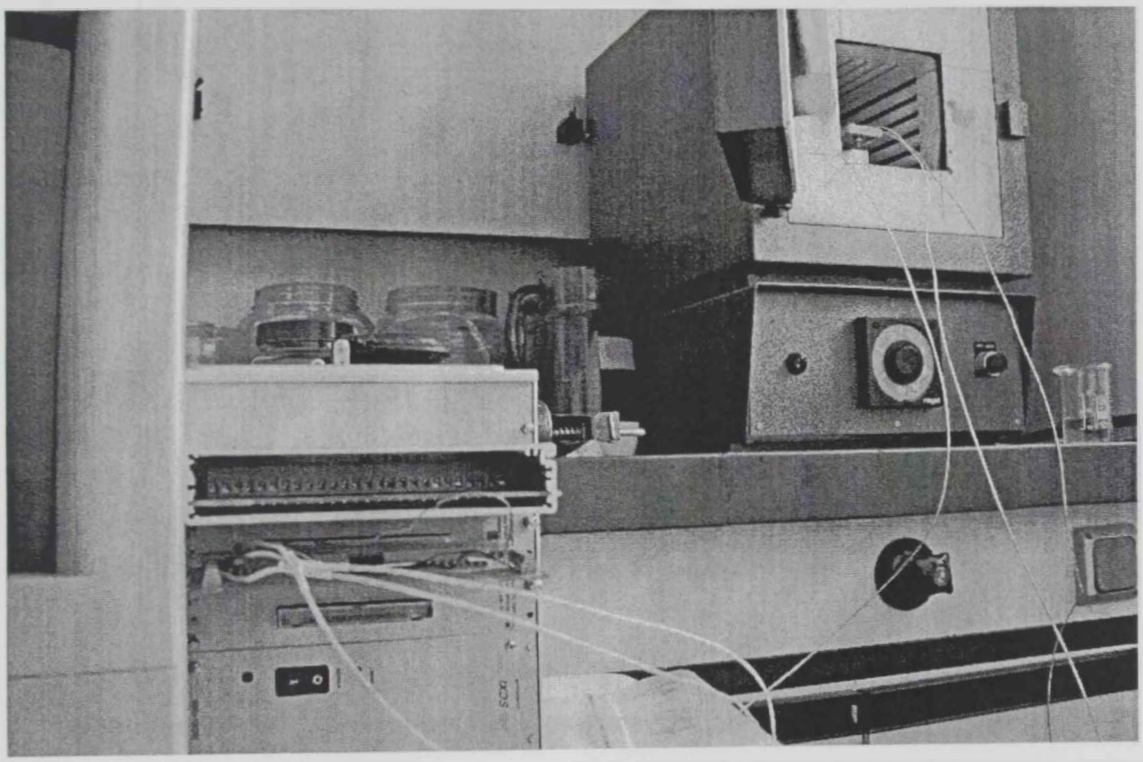

Figure 5.20: Thermocouples attached to data acquisition system

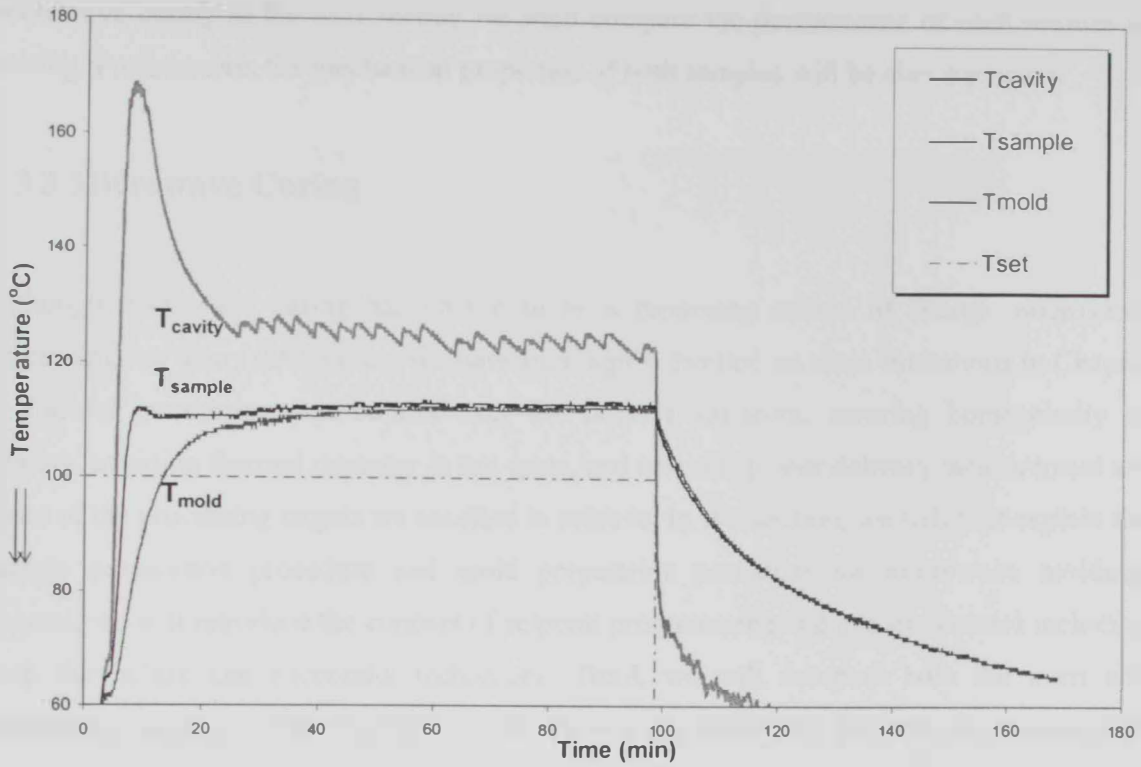

Figure 5.21: Heating Profile of isothermal oven cure cycle

B- Oven cavity had a temperature overshoot to around 170 °C until it stabilized to 130 °C. The time required to achieve stability was about 20 minutes.

C- Both mold and sample temperature reached around 112 °C despite the fact that the resin ramp rate is faster than the aluminum mold. Possible reason for the high sample ramp rate is the chemical exotherm of the resin which accelerates the heating process. This is a more likely explanation bearing in mind that the samples were kept at room temperature until gelation took place. In addition, much time was required to stabilize the temperature of the sample, about 10 minutes.

D- Temperature variations in cavity, mold, and resin clearly demonstrate the thermal gradient in the system. Temperature difference of 18 °C was found between the cavity and the sample.

In conclusion, oven curing has showed several drawbacks. Slow heating, thermal gradient, and set temperature inaccuracy are the main sources of limitations. After introducing

microwave curing in the next section we shall compare the performance of each sources of heating. Furthermore, the mechanical properties of both samples will be also discussed.

5.3.3 Microwave Curing

Although microwave curing has proven to be a promising source of energy, microwave processing has many difficulties. We have thoroughly dwelled on these limitations in Chapter 2. Careful monitoring and control over the process variables, assuring homogeneity of heating, avoiding thermal runaway & hot spots, and accurate power delivery measurement are some of the processing targets we excelled to achieve. In this section, we will first explain the sample preparation procedure and mold preparation particular for microwave molding. Second, we will introduce the concept of setpoint programming and process control including both the failure and successful techniques. Third, we will compare both the oven and microwave curing results. Fourth, we will discuss our efforts to improve the process and optimize the performance of microwave curing on two levels, sample preparation and variation of process parameters. Fifth, we will compare between the different curing conditions chosen by mechanically testing the cured samples of both oven and microwave processing. Finally, we shall draw conclusions on the best curing scenarios and recommend future testing plans.

5.3.3.1 Sample Preparation

Sample preparation containing mixing, stirring, degassing and molding is similar to the explanation of oven curing. However, a key difficulty had to be overcome. To prevent electromagnetic interference in temperature measurement, a shielded platinum thermocouple was used which is relatively inflexible and can not be inserted from the top of the mold. Therefore, the thermocouple had to be first inserted from the side of the Teflon mold as seen in [Figure 5.22]. Otherwise, the liquid resin will leak extensively if the thermocouple is to be inserted after filling. The opening size is made 1 mm more than the thermocouple diameter to seize leakage and at the same time facilitate trouble-free insertion and removal. The thermocouple also had to be covered with release agent to further assist the extraction after sample curing. This preparation stage definitely delayed the one sample molding process. From Figure 5.22 we can also observe that the thermocouple is inserted at one end of the

sample. This was necessary so that enough material remains undamaged for later flexural testing.

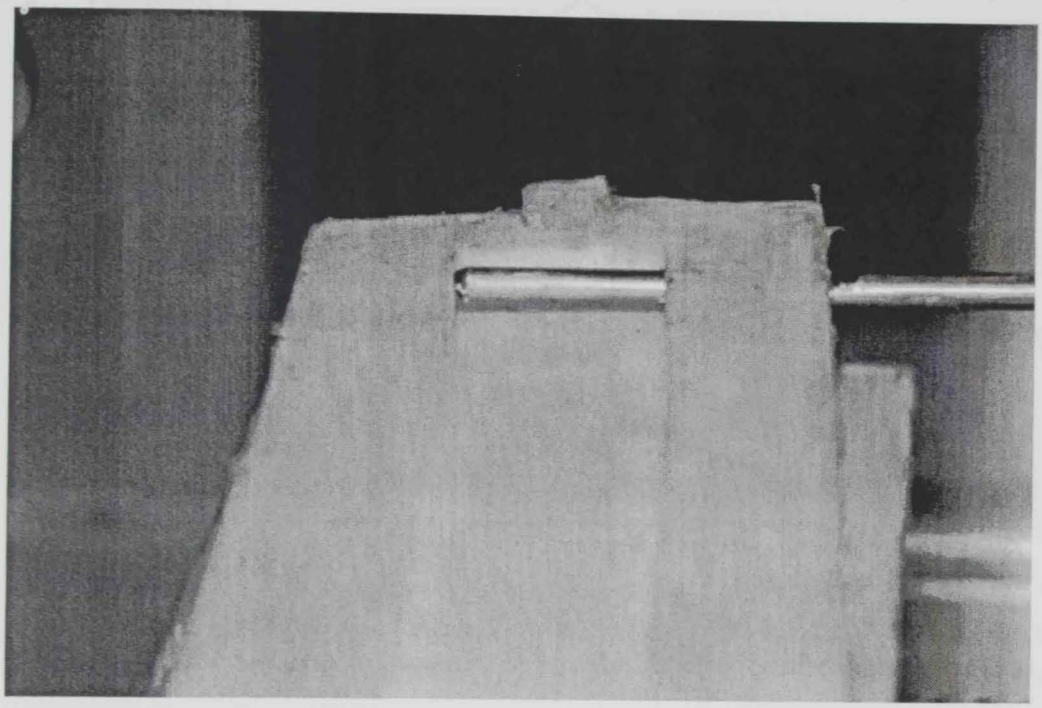

Figure 5.22: Shielded thermocouple insertion prior to filling

5.3.3.2 Setpoint Programming

Prior to sample preparation, the microwave controller has to be programmed to include the specified isothermal curing cycle. The programming is carried out using the itools® Software Version 4 from Eurotherm®. The control techniques used in the testing is setpoint programming. Generally speaking, the setpoint (SP) may be temperature, pressure, light level, humidity, etc., depending on the application. In our case, the setpoint is referred to the set temperature during processing. The controller applies numerous algorithms to assure that the process variable (PV) or actual temperature coincides with setpoint temperature. The Program is divided into a flexible number of segments, each being single time duration and containing details for each profiled setpoint. Figure 5.23 demonstrates a schematic program in which the setpoint varies with time in each segment. The total number of segments available is 100 per program. The controller can save up to 20 different programs. (Engineering Handbook Chapter 6, 2002).

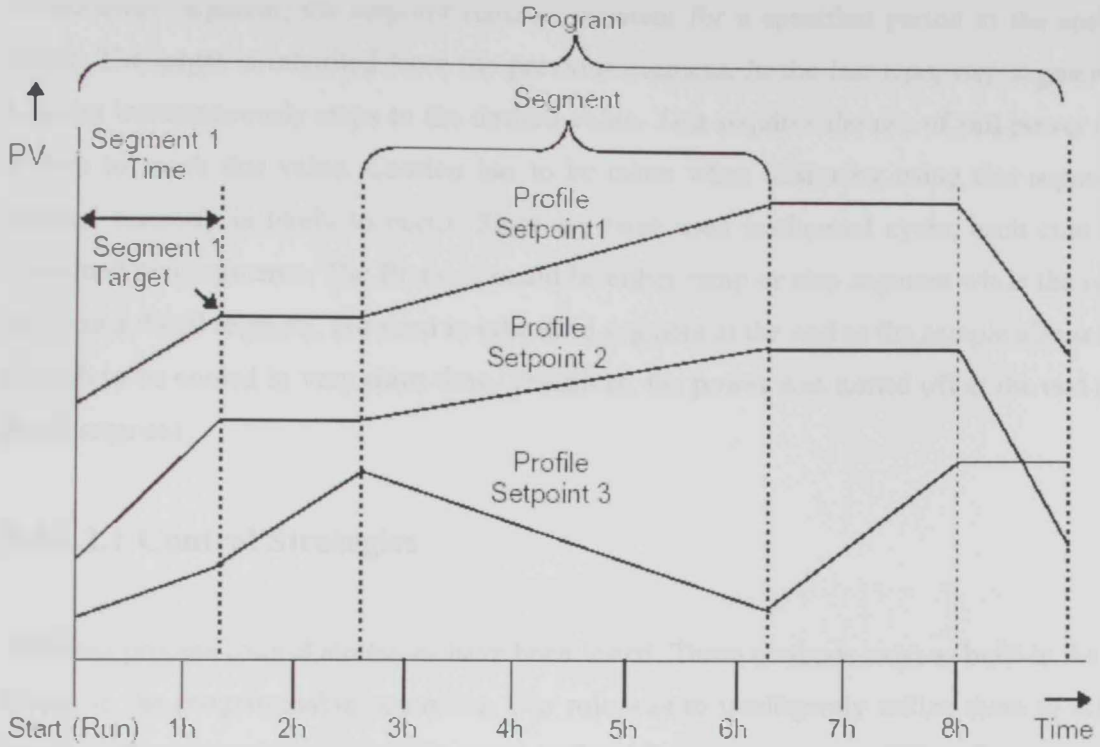

Figure 5.23: Segments of Setpoint Programming (Engineering Handbook Ch6, 2002)

Three types of segments can be chosen to construct the program, ramp, dwell, and step. Figure 5.24 is a typical representation of each. In the ramp segment, the setpoint ramps linearly to a target value, either at a set rate in what so called ramp-rate programming, or in a set time in what is called time-to-target programming. You must specify the ramp rate or the ramp time, and the target setpoint, when creating or modifying a program.

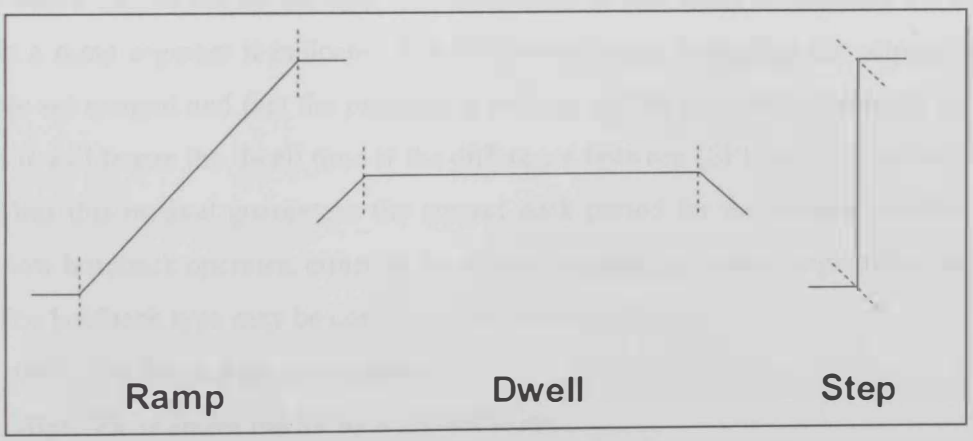

Figure 5.24: Types of Segments in Setpoint Programming

In the dwell segment, the setpoint remains constant for a specified period at the specified target. The target is inherited from the previous segment. In the last type, step segment, the setpoint instantaneously steps to the desired value. This requires the use of full power of the system to reach this value. Caution has to be taken when designing using this segment as thermal runaway is likely to occur. Since we have used isothermal cycle, each cure cycle contained two segments. The first one could be either ramp or step segment while the second one was a dwell segment. No need to take third segment at the end as the sample size is small enough to be cooled in very short time. Therefore, the power was turned off at the end of the dwell segment.

5.3.3.2.1 Control Strategies

Different process control strategies have been tested. These methods exist as built-in function blocks in the programmable controller. Our role was to intelligently utilize them to achieve the desired goal, optimization of the cure cycle. After testing many of these function blocks we selected the two most significant ones. We assessed the performance of each and selected the method that efficiently satisfies the desired isothermal cure cycle.

5.3.3.2.1.1 Holdback Control

The first method is the holdback technique or in other words "guaranteed soak" technique. Holdback freezes the program if the process value (PV) does not track the setpoint (SP) by an amount which can be set by the user. It can operate in two types of segment the ramp and dwell. In a ramp segment it indicates that the process value is lagging the setpoint by more than a pre-set amount and that the program is waiting for the process to catch up. In a Dwell segment it will freeze the dwell time if the difference between (SP) and (PV) exceeds pre-set limits. Thus this method guarantees the correct soak period for the sample. Holdback Type defines how holdback operates, either in the whole program, or in each segment as configured above. The holdback type may be configured in four modes:

- OFF: Holdback does not operate.
- High: PV is above the SP by a pre-set value.
- Low: PV is below the SP by a pre-set value.
- Band: PV is above or below the SP by a pre-set value.

As a first attempt to examine the accuracy of holdback technique, we have used again water samples, being a perfect microwave heating material with well known dielectric properties. Another reason for using water is the fact it will present an extra challenge for the controller as it has instantaneous heating capability as that shown in chapter 2.

The input data needed for holdback technique is the following: Segment type, target temperatures, holdback mode, and permissible deviation temperatures. Two combinations of these settings has been formed and tested as shown in Table 5.6.

Table 5.6: Holdback Settings of Water Samples

Set #	1st Seg.	2nd Seg.	Dwell Temp	Dwell Time	Holdback Mode	Holdback Value
1	Step	Dwell	75 °C	30 min	High	0 °C
2	Step	Dwell	75 °C	5 min	Band	3 °C

From this table, we can see that two segments are used for the program of each combination, step and Dwell. The first step segment is to assure highest heating rate possible and the second is a dwell segment at 75 °C for different durations. Furthermore, two modes of holdback were used. The High mode has a preset value of zero which suggests complete matching of the set temperature. The band mode of the second set, however, has a preset value of 3 °C above and below the isothermal temperature, or 6 °C total range.

Figure 5.25 shows the microwave heating of water samples using set #1. As soon as heating starts the controller works with 100% power to satisfy the step heating to 75 °C. It reduces the output power gradually to prevent thermal runaway. However, a 10 °C overshoot is observed at the beginning of the dwell segment. Nevertheless, while the dwell temperature is supposed to be 30 min as seen in the "Dwell Segment" legend in the table, the "holdback Segment" was further increased to around 50 min dwell. This is due to the fact that the controller holds or freezes the program until the temperature comes back to exactly match the set temperature which extensively increases the total time of dwell segment. Therefore, we tried to increase the tolerance to be 3°C above and below the set temperature to reduce the lag between actual holdback and the theoretical dwell segment. Such modification can be seen for set #2 in

Figure 5.26. While the thermal overshoot is significantly reduced, the delay between the 5 minutes dwell and the actual holdback segment is still obvious. The reason for this phenomenon is the fact that the controller decreased the microwave power relatively slower than set #1 which made the 3 °C band partially ineffective. Figure 5.27 further clarifies this point by showing the time where the program is frozen to decrease the system temperature below the 3 °C band.

In short, the holdback method has proven to be ineffective on controlling and homogenizing the sample temperature. We have to investigate other methods such as the coming PID control method.

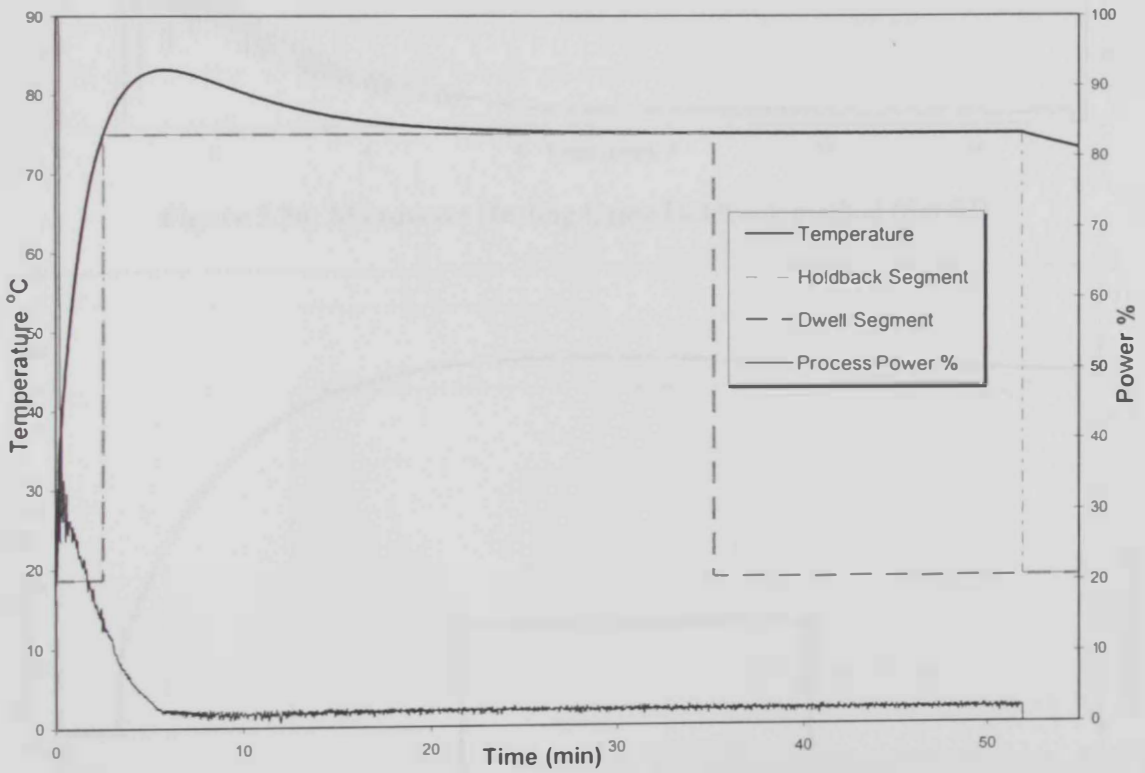

Figure 5.25: Microwave Heating Using Holdback method (Set #1)

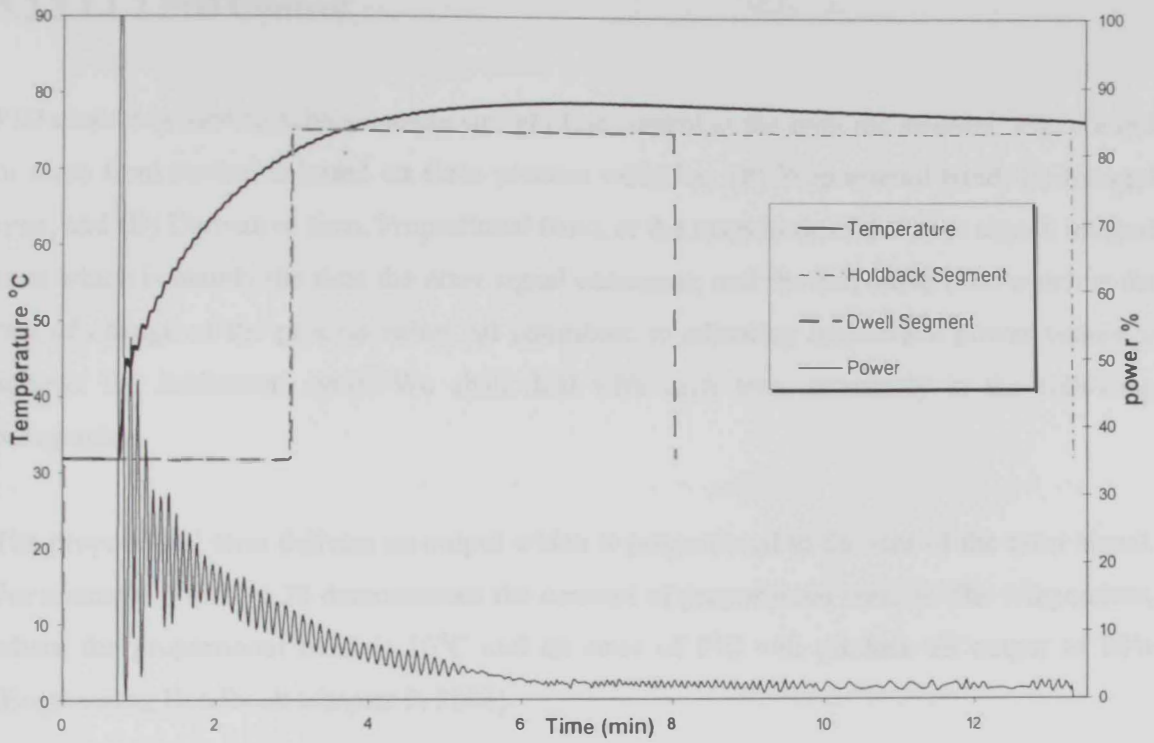

Figure 5.26: Microwave Heating Using Holdback method (Set #2)

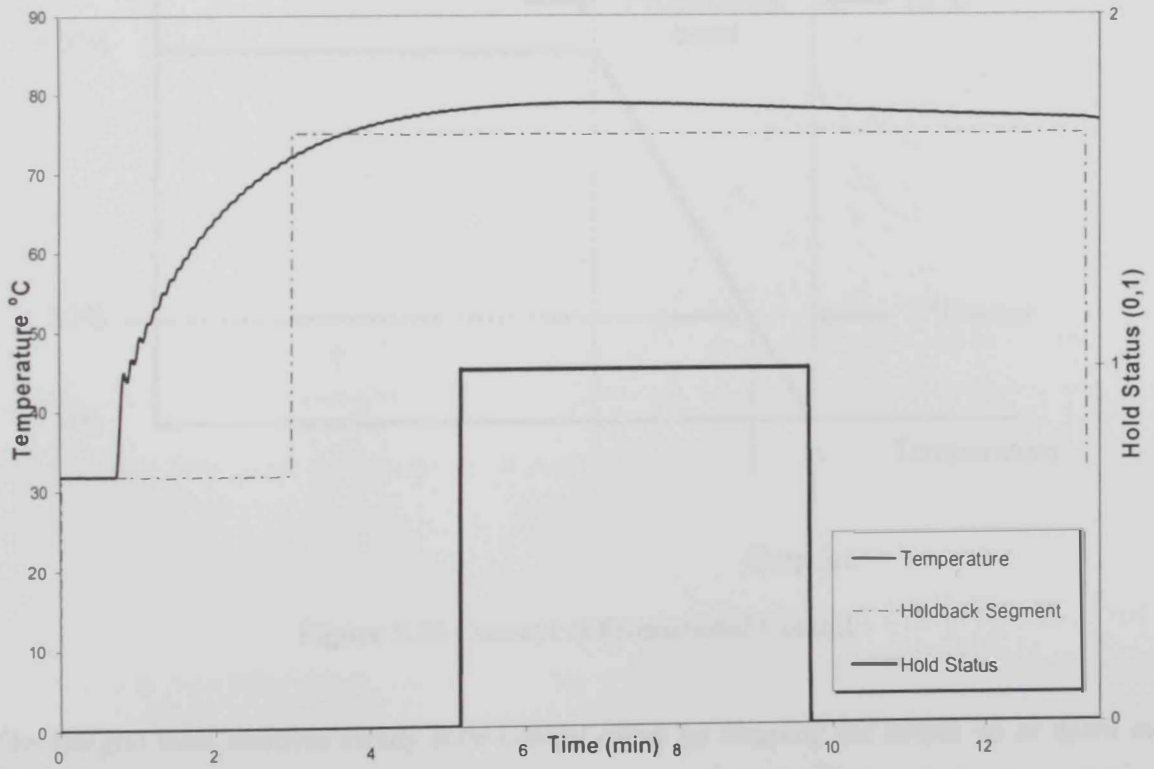

Figure 5.27: Holdback Status during Microwave heating of Water (Set #2)

5.3.3.1.1.2 PID Control

PID control is used to achieve stable straight line control at the required setpoint. PID control or three term control is based on three process variables: **(P)** Proportional band, **(I)** Integral time, and **(D)** Derivative time. Proportional band, or the magnitude of the error signal, integral time which is mainly the time the error signal consumes, and the derivative time which is the rate of change of the process value, all contribute to adjusting microwave power values to achieve the isothermal cycle. We shall deal with each term separately in the following paragraphs.

The proportional term delivers an output which is proportional to the size of the error signal. For example, Figure 5.28 demonstrates the concept of proportional control. The temperature, where the proportional band is 10°C and an error of 3°C will produce an output of 30% (Engineering Handbook Chapter 9, 2002).

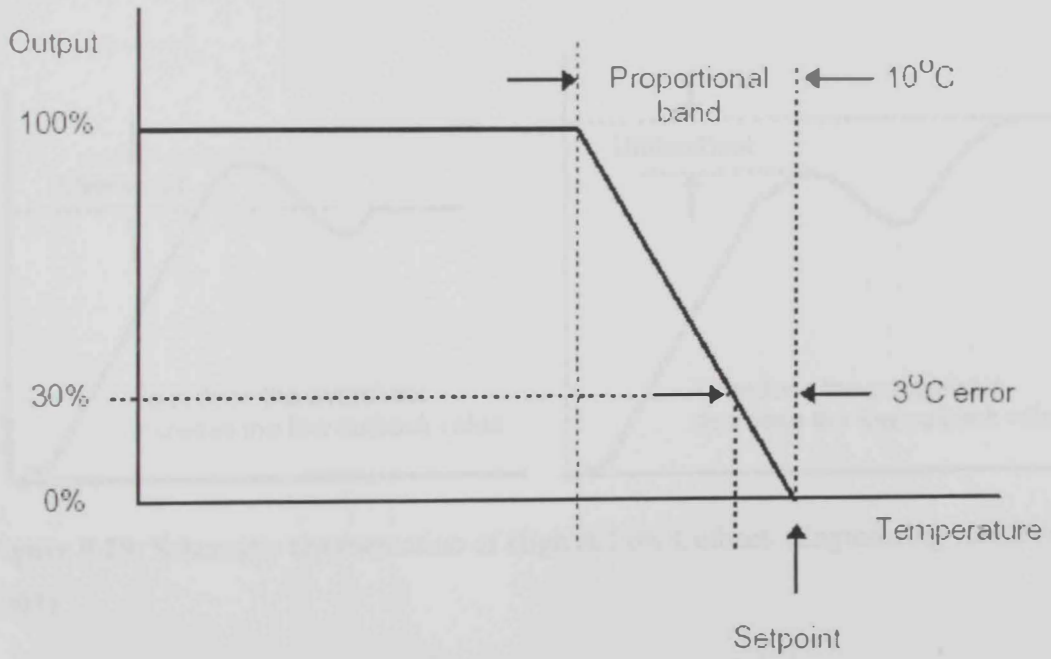

Figure 5.28 Concept of Proportional Control

The integral term removes steady state control offset by ramping the output up or down in proportion to the amplitude and duration of the error signal. The ramp rate is the integral time constant, and must be longer than the time constant of the process to avoid oscillations.

The derivative term is proportional to the rate of change of the temperature or process value. It is used to prevent overshoot and undershoot of the setpoint by introducing a preventive action. In addition, if the process value falls rapidly, an oven door being opened during operation as an example, the derivative term modifies the proportional band according to this rate of change having the effect of narrowing the proportional band. Derivative action, therefore, improves the recovery time of a process automatically when the process value changes rapidly. In our case the derivative term is calculated based on the temperature variation with time. It is used to prevent thermal shocks caused by sudden change of output.

Other important terms that support the function of PID control is the high and low cutback. While the PID parameters are optimized for steady state control, high and low cutback parameters are used to reduce overshoot and undershoot for large step changes in the process as shown in Figure 5.29. They respectively set the number of degrees above and below setpoint at which the controller will start to increase or cutback the output power.

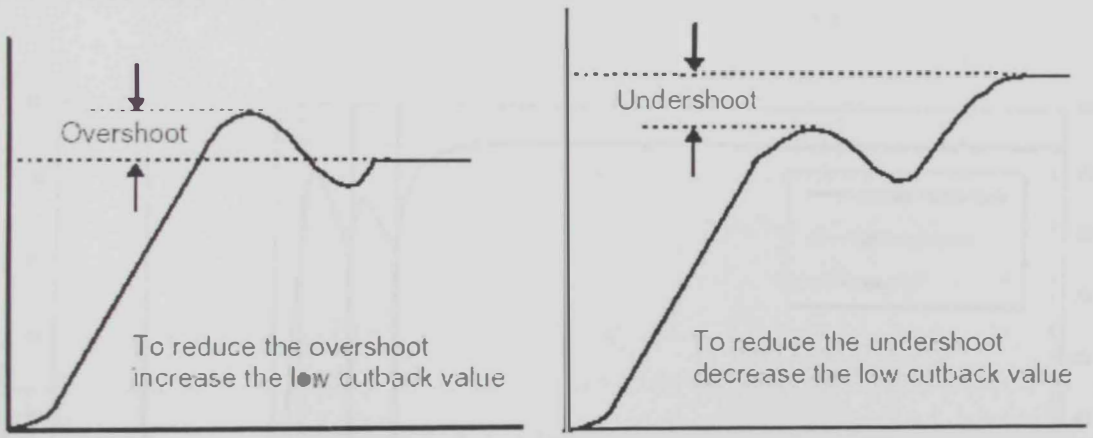

Figure 5.29: Schematic representation of High & Low Cutback (Engineering Handbook Ch9, 2002)

After explaining the different processing variables that should be set in PID control system, the question remaining is how we can find the optimum values of these terms. Since trial and error is usually a time-consuming operation, we should develop a tuning strategy to obtain the value of Proportional term, integral term, derivative term, and High & Cutback terms. The tuning process can be defined as the matching of the controller characteristics to the particular

characteristics of the desired cure cycle. As a general guideline a well tuned process have the following features:

A- Stable, 'straight-line' control of the temperature at setpoint without fluctuation.

B- No overshoot, or undershoot, of the temperature setpoint.

C- Quick response to deviations from the setpoint caused by external disturbances, thereby rapidly restoring the temperature to the setpoint value.

The microwave controller uses a one-shot auto tuning process which automatically sets up the initial values of the parameters explained above. The one-shot tuner works by switching the output on and off to induce an oscillation in the measured value. From the amplitude and period of the oscillation, it calculates the tuning parameter values. The measured value must oscillate to some degree for the tuner to calculate the PID values. This process was carried out on both water and epoxy samples. Since water is to be used in calibration process, previously explained, the tuning process is inevitable to assure reliable results. Figure 5.30 and Figure 5.31 shows the variation of process variables during the auto tuning process of water and epoxy respectively.

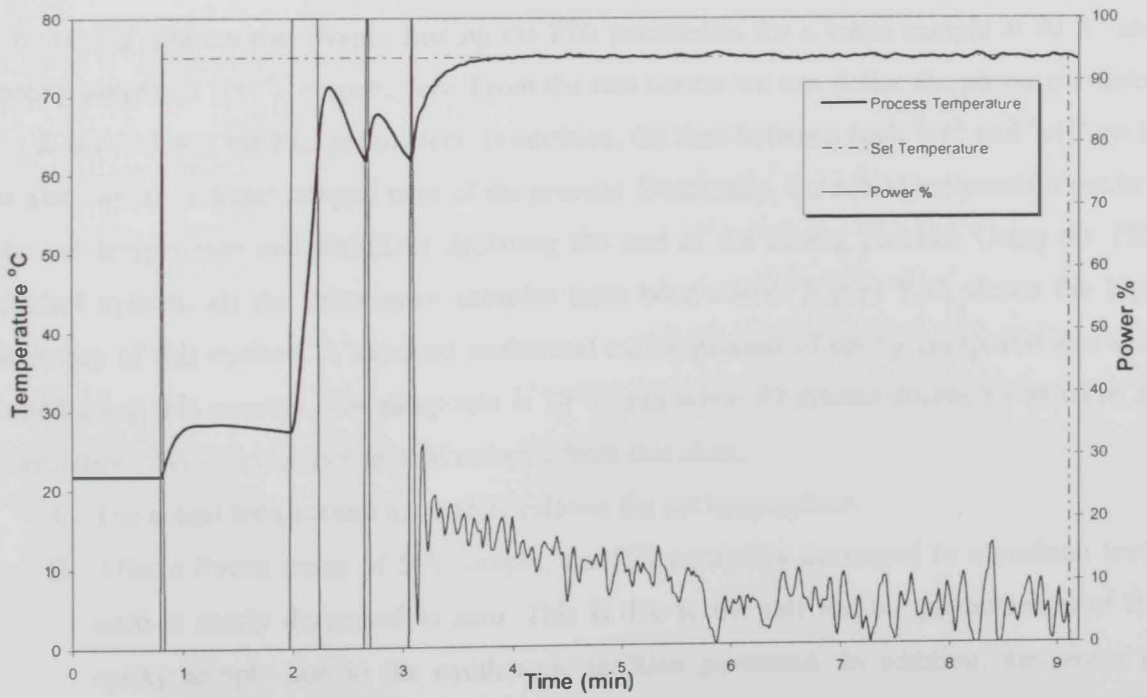

Figure 5.30 Autotuning Process of Water Samples

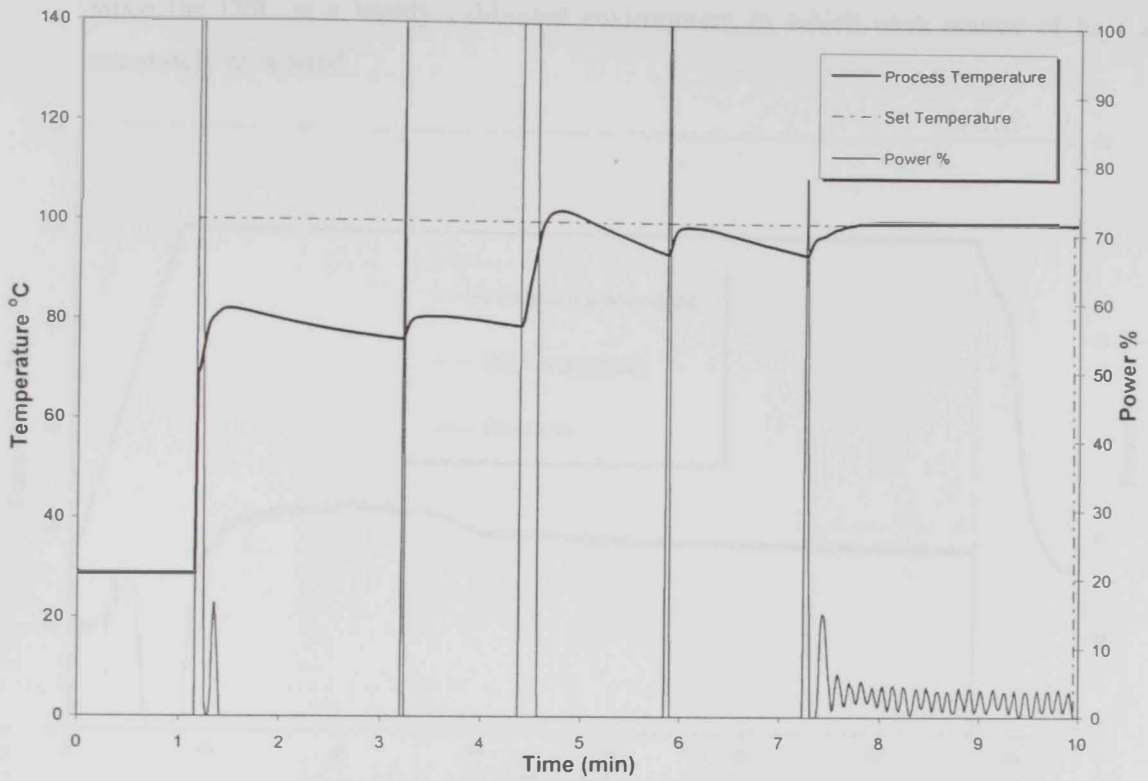

Figure 5.31 Autotuning Process of Epoxy Samples

The tuning process was simply finding the PID parameters for a water sample at 60 °C and epoxy sample at 100 °C respectively. From the two curves we can notice the power oscillates on & off to detect the PID parameters. In addition, the time between each "on" and "off" cycle is also varied to detect integral time of the process. Eventually, the actual temperature reaches the set temperature and stabilizes declaring the end of the tuning process. Using the PID control system, all the microwave samples have been cured. Figure 5.32 shows the high accuracy of this method. A standard isothermal curing process of epoxy composite was auto tuned using this concept. The ramp rate is 10 °C/min while 60 minute duration was taken as dwell time. We can observe several remarks from this chart:

A- The actual temperature accurately follows the set temperature.

B- After a Power pulse of 50% output, the PID controller decreased to a medium level until is nearly decreased to zero. This is due to the self heating phenomenon of the epoxy sample due to the exothermic reaction generated. In addition, the power is diminished in order to prevent thermal runaway at the start of the dwell segment. By inverting the power cycle of the cure process, we could get a curve quite similar to DSC exothermic curve. However, exact comparison of this curve will not be feasible

since the DSC is a highly calibrated environment in which each source of heat is accurately measured.

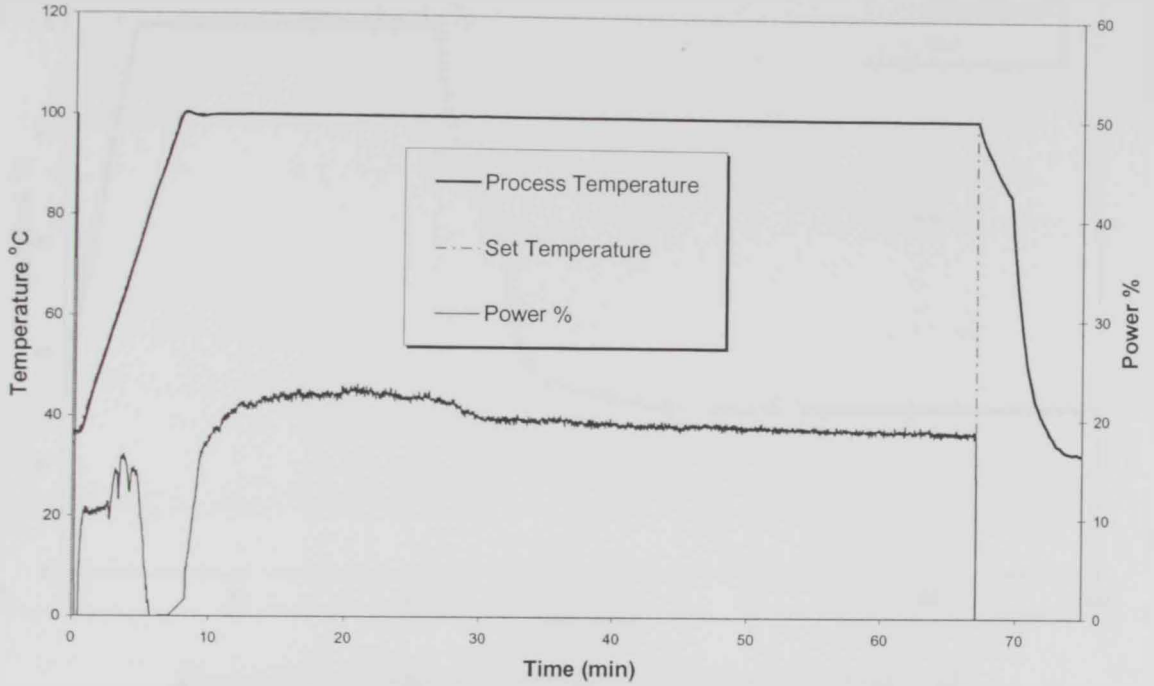

Figure 5.32 PID control of epoxy isothermal cure cycle

5.3.3.3 Comparison to Oven Curing

After clearly demonstrating the applicability of PID control, it is worth while comparing the performance of oven curing with microwave curing on the basis of cure cycle homogeneity and prevention of thermal runaway. An isothermal curing process with a 10 °C ramp rate and 30 minutes dwell time was applied for oven and microwave curing. Figure 5.33 clarifies this comparison. While microwave cured sample perfectly matched the isothermal cycle, a 10 °C deviation is observed in the oven cycle with minor overshoot at the beginning of the dwell segment.

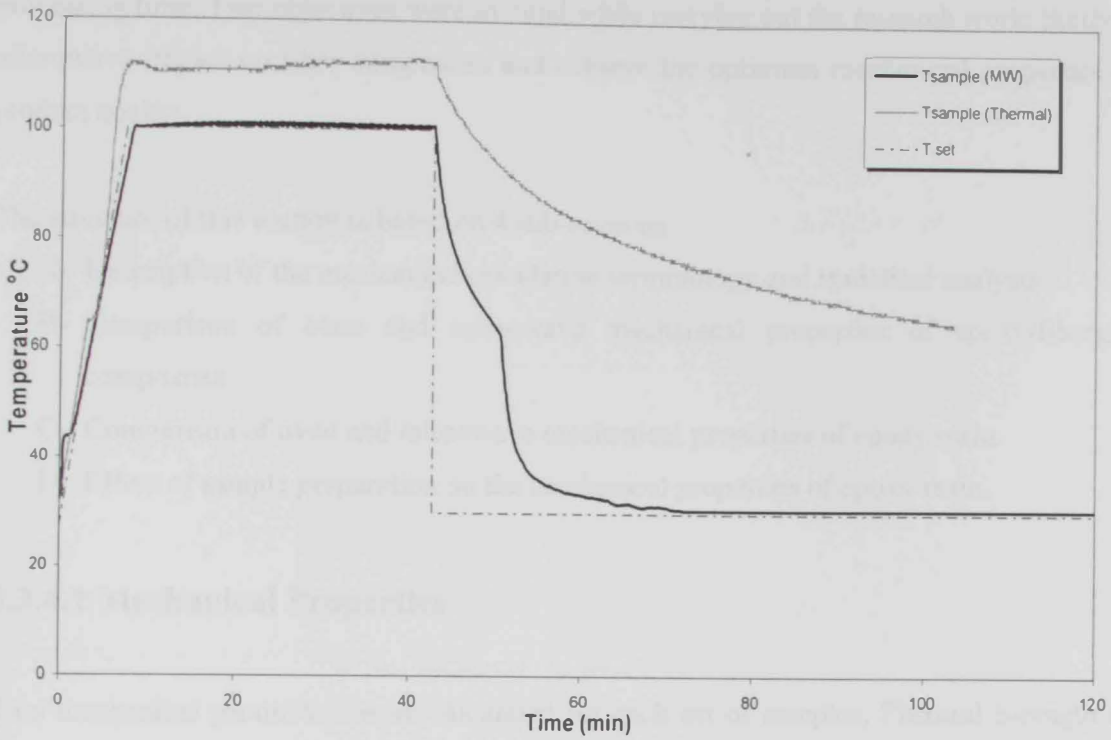

Figure 5.33: Comparison of Oven and Microwave Curing Cycle

5.3.4 Optimization Approach

This section is considered the most unique experimental section of the thesis research. After examining different curing methods and techniques we needed to research on the best combination of segment type and cure time to achieve the highest mechanical properties. First, we compared the mechanical properties of a standard isothermal cure cycle, recommended by Dow Chemicals, for oven and microwave curing. Please refer to table 4.1 for more details. Afterwards, we have developed a testing plan consisting of 10 groups of samples including neat resin and fiberglass composites. Each group of settings consisted of 5 samples with the same condition. Heating rate as low as 10 °C/min and as high as 200 °C/min was also inspected. Dwell time was modified to include 60, 30, 20, and 13 min which is the minimum time recommended by DSC at 100 °C. Sample preparation was also inspected such as vacuum degassing and room temperature gelation and the effect on the final mechanical properties was analyzed. All the microwave processing was done using the PID control method while thermal curing was carried out using the oven setup. Due to the fact that cure rate is a function of temperature as was explained in the kinetic analysis, we have fixed the isothermal temperature to 100 °C. This was essential to independently study the effect of

processing time. Two objectives were in mind while carrying out the research work: Study the microwave impact on fiber composites and achieve the optimum mechanical properties and product quality.

The structure of this section is based on 4 sub-sections:

A- Description of the mechanical calculation terminology and statistical analysis.

B- Comparison of oven and microwave mechanical properties of epoxy/fiberglass composites.

C- Comparison of oven and microwave mechanical properties of epoxy resin.

D- Effect of sample preparation on the mechanical properties of epoxy resin.

5.3.4.1 Mechanical Properties

Two mechanical parameters were calculated for each set of samples, Flexural Strength and Flexural modulus. Flexural strength was calculated as follows:

$$\sigma_f = \frac{3PL}{2bd^2} \qquad (5.13)$$

Where :

σ_f = stress in the outer fibers at midpoint, MPa,

P = Maximum load on the load-deflection curve, N,

L = support span, mm,

b = width of sample tested, mm,

d = depth of sample tested, mm.

Flexural Modulus or modulus of elasticity, on the other hand, was calculated as follows:

$$E_B = \frac{L^3 m}{4bd^3} \qquad (5.14)$$

Where:

E_B = bending modulus of elasticity, MPa,

L = support span, mm,

b = width of sample tested, mm,

d = depth of sample tested, mm,

m = slope of the tangent to the initial straight-line portion of the load-deflection curve, N/mm.

For statistical analysis, the standard deviation and the average deviation of data points were calculated as follows:

$$S = \sqrt{(\sum X^2 - n\overline{X}^2)/(n-1)} \qquad (5.15)$$

$$A = \sum \left| X - \overline{X} \right| / n \qquad (5.16)$$

Where:

S = estimated standard deviation, MPa,

A = estimated average deviation, MPa,

X = value of single observation of strength or modulus, MPa,

$\overline{X}$ = arithmetic mean of observation set, MPa,

n = number of observations

5.3.4.2 Behavior of Fiber glass Composites

Table 5.7 shows the behavior of glass fiber/epoxy composites cured by oven and microwave energy at different dwell time. The heating rate was common for all to be 10 °C/min. The data in brackets is for standard deviation of flexural strength (S_σ) and modulus (S_E).

Table 5.7: Mechanical Properties of Glass Fiber/Epoxy Composites cured at 100 °C

Material	Method	Dwell Time (min)	Flexural Strength (MPa)		Flexural Modulus (GPa)	
			σ_F (S_σ)	A_σ	E_F (S_E)	A_E
GF/Epoxy	Oven	60	209.75 (4.19)	3.41	8.33 (0.65)	0.52
	Microwave	60	228.68 (4.21)	3.37	9.07 (0.39)	0.34
		30	226.28 (4.35)	3.49	9.03 (0.48)	0.37

From this figure several remarks can be deduced:

A- For the recommended 60 minutes cure cycle of Dow chemicals, the microwave strength has increased from 209.75 to 228.68 MPa. Same trend observed for modulus to increase from 8.33 to 9.07 GPa. Microwave curing has relatively improved the mechanical properties of the composites. This can be explained as microwave heating is more homogeneous than thermal curing by elimination of thermal runaway and thermal gradient. The alignment of the epoxy chains boosted the system crystallinity. This explanation was interpreted by the work of several researchers such as Bai et al. (1995) and Zhou et al. (2003).

B- Decreasing the dwell time by 50% resulted in the microwave samples maintaining similar mechanical properties. This finding highlights the need to investigate the full microwave capability to reduce curing time.

C- Good reliability was obtained in the data knowing that the average deviation of flexural strength ranges from 3.37-3.49 MPa for flexural strength and from 0.34-0.52 for the flexural modulus.

As we mentioned in section 2.2.1 the dielectric properties of fiber glass composites are dominated by the dielectric loss of the resin rather than the fiber. This is due to the microwave "transparency" of fiber glass. Therefore, after we have compared the mechanical properties of oven and microwave heating of composites we concentrated on optimizing the cure behavior of the epoxy resin itself. This has also lead us to more focused study by separating the drawbacks of hand lay-up method, such as entrapped air bubbles, from the mechanical testing data.

5.3.4.3 Behavior of Epoxy Resin

Table 5.8 shows the mechanical properties of epoxy resin. Different ramp rates and dwell time have been tested. A standard oven cycle was tested against 5 different combinations of microwave cycle.

Table 5.8: Mechanical Properties of Epoxy Resin cured at 100 °C

Material	Method	Ramp Rate (°C/min)	Dwell Time (min)	Flexural Strength (MPa)		Flexural Modulus (GPa)	
				σ_F (S_σ)	A_σ	E_F (S_E)	A_E
Epoxy Resin	Oven	10	60	71.03 (1.2)	0.92	1.98 (0.14)	0.10
	Microwave	10	30	74.54 (2.21)	1.47	2.17 (0.2)	0.16
		10	20	76.6 (2.4)	1.86	2.01 (0.16)	0.12
		10	13	75.4 (3.1)	2.40	2.08 (0.37)	0.26
		200	20	-	-	-	-
		200*	20	77.05 (1.58)	1.24	2.27 (0.31)	0.21

* Power Varied during cure

The following remarks were deduced:

A- Again we can see that the flexural strength and modulus for microwave curing have exceeded the values in oven curing. Same explanation as fiber reinforced composites is applicable here.

B- For microwave curing at 10 °C/min heating rate and dwell time were varied from 13-30 minutes, we can see no sharp changes in strength or modulus. This highly supported the credibility of DSC testing. Back to degree of cure chart, figure 5.3, at 100 °C epoxy reaches maximum degree of cure at 13 minutes. Earlier in the literature review chapter we quoted similar finding by Nightingale & Day (2002). By varying the cure time of epoxy/fiber glass composite from 5-40 minutes they found similar flexural properties. This finding also supports the necessity of DSC analysis to optimize the process. Figure 5.34 better visualized this effect. In this figure the average deviation error bars were also plotted. It shows that the deviation from average is higher as the material approaches the 13 minutes. Similar trend is observed in Figure 5.35 for the flexural modulus. This is expected since the 13 minute is a critical point below which the material starts to decrease in strength quickly. Therefore, any slight error in time measurement could lead to decrease in the value of the strength of the resin. Nonetheless, this time duration was measured by a highly calibrated device with minimum level of heat losses.

C- As part of optimization approach, we tried to make use of the maximum heating rate obtainable by the controller and at the same time avoiding thermal runaway. A 200 °C/min heating rate was used. As we can see in the first 200 °C/min heating rate row in the table, no data were recorded. This is due to the failure of the controller to stabilize the temperature as thermal runaway took place. Figure 5.36 shows the cure behavior of the failed sample. Maximum power is applied in a "step" segment to achieve the 200 °C/min. The sample absorbed higher energy that it could diffuse away. The result was a temperature overshoot despite the fact that the power was turned instantaneously to zero. The phenomenon was further boosted by the high exothermic reactions of the cure process. Figure 5.37 shows the failed specimen. A possible analysis for the failure condition of the specimen is the rapid evaporation of the diluent in the resin as it couples with the microwave energy. This lead to the gaseous bubbling observable in the figure.

D- In order to prevent thermal runaway at this extreme condition, we tried to reduce the maximum possible power to 30% only with the same "step" segment of 200 °C/min. Figure 5.38 shows the heating profile at this condition. Although a minor temperature deviation of 10 °C was observed the sample obtained was defect free. This is verified by the flexural strength of the cured samples, 77 MPa, which coincides with the average strength of the epoxy resin.

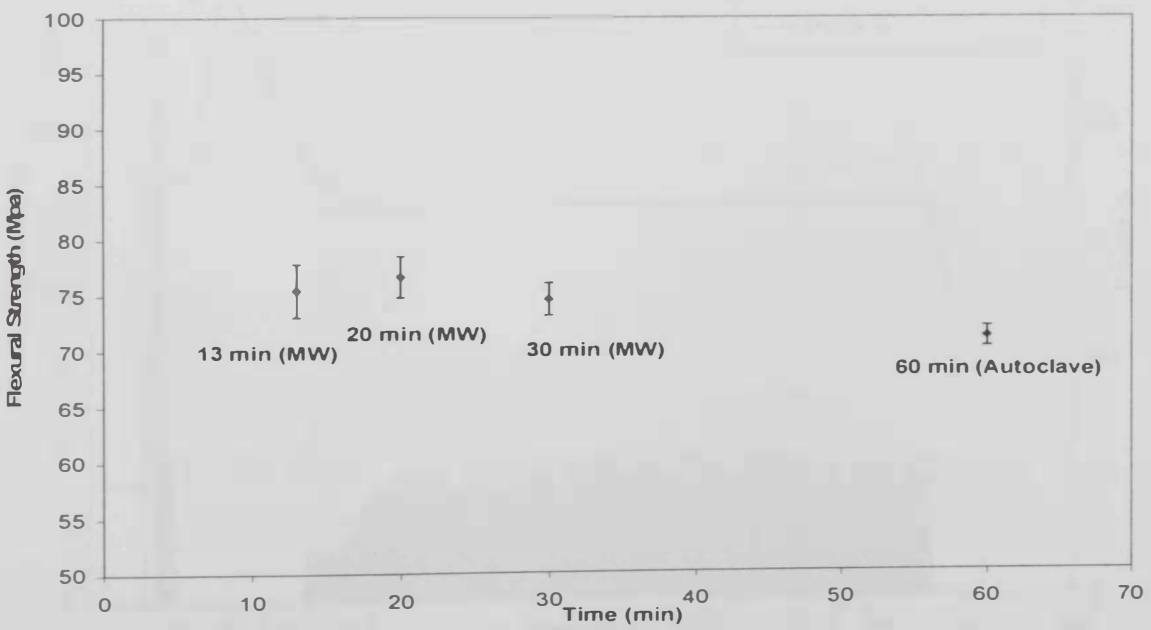

Figure 5.34: Effect of dwell time on the flexural strength of epoxy samples

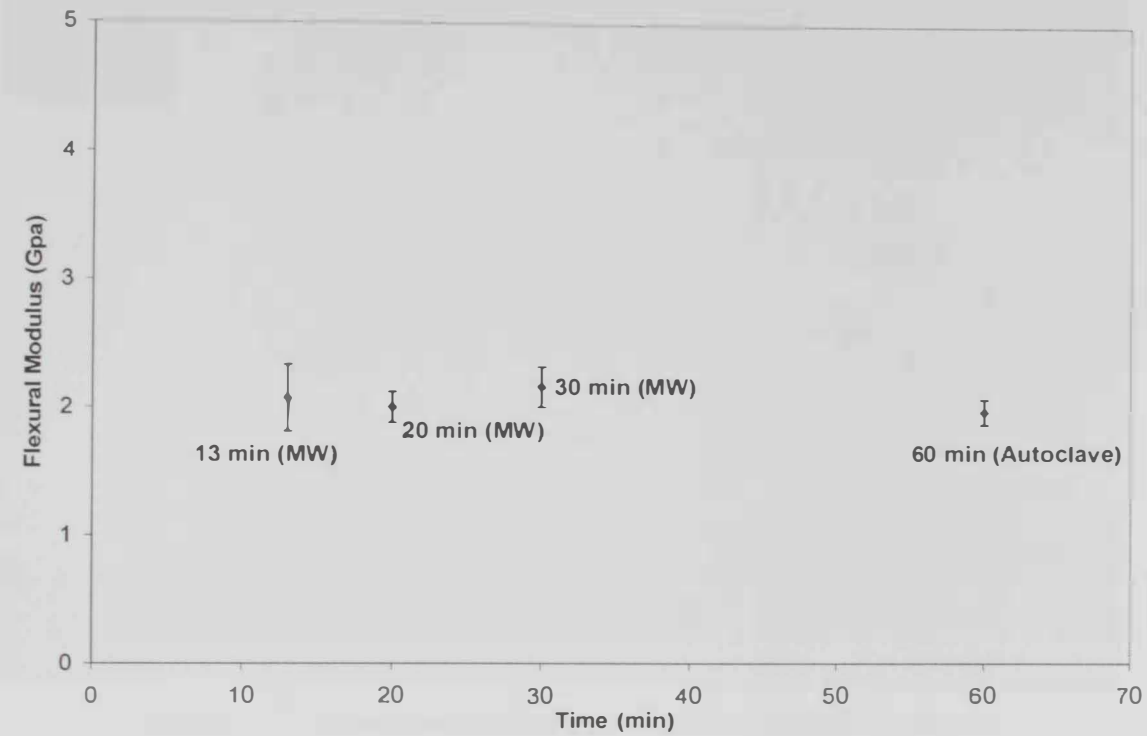

Figure 5.35: Effect of dwell time on the flexural modulus of epoxy samples

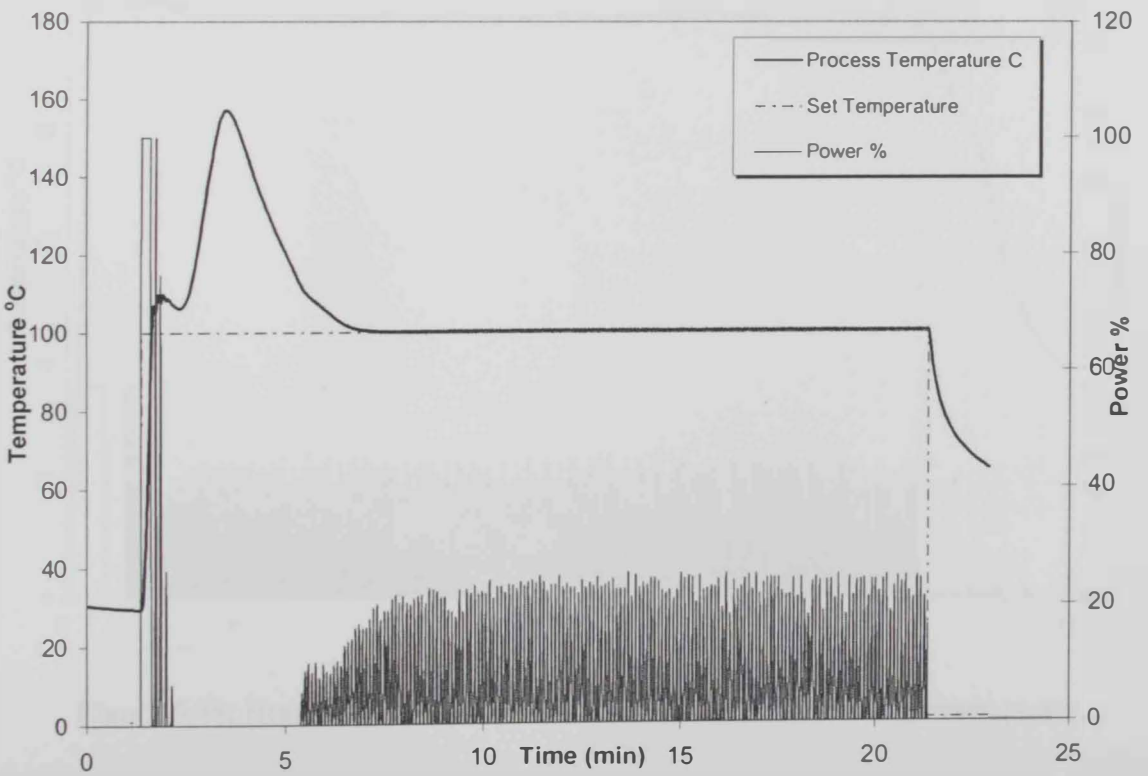

Figure 5.36: Thermal runaway of epoxy sample at 200 °C/min heat rate

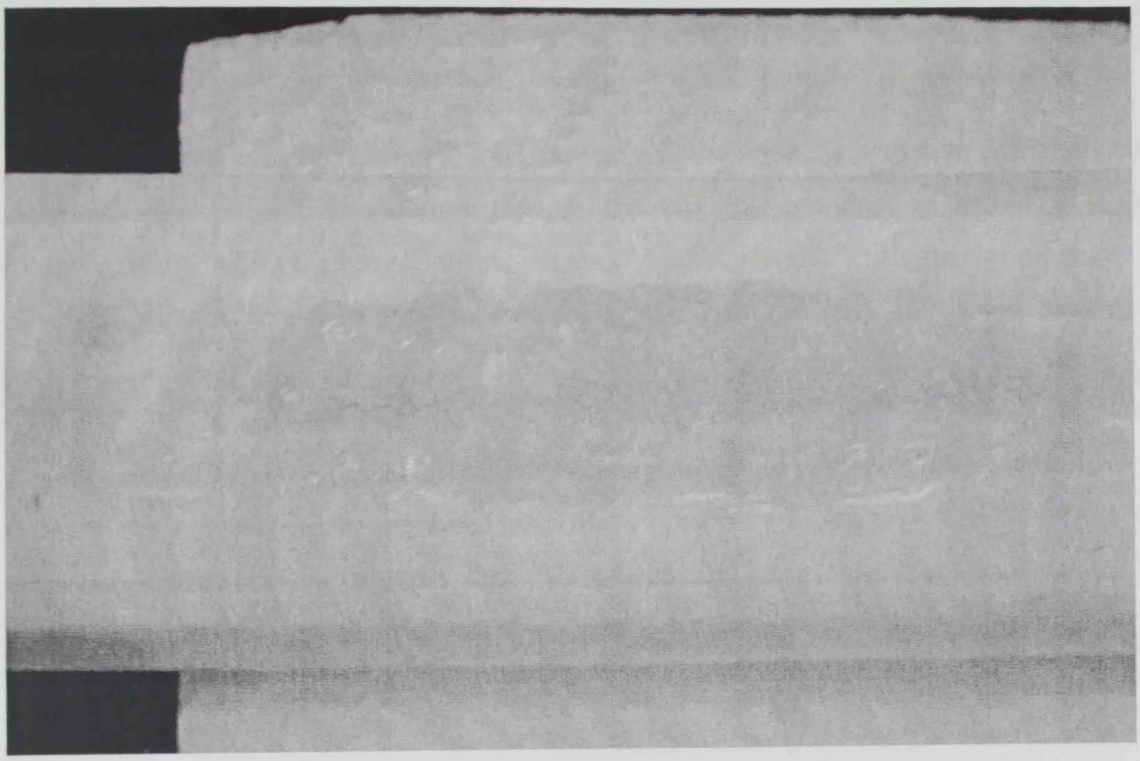

Figure 5.37: Failed Sample of epoxy resin at 200 °C/min heating rate

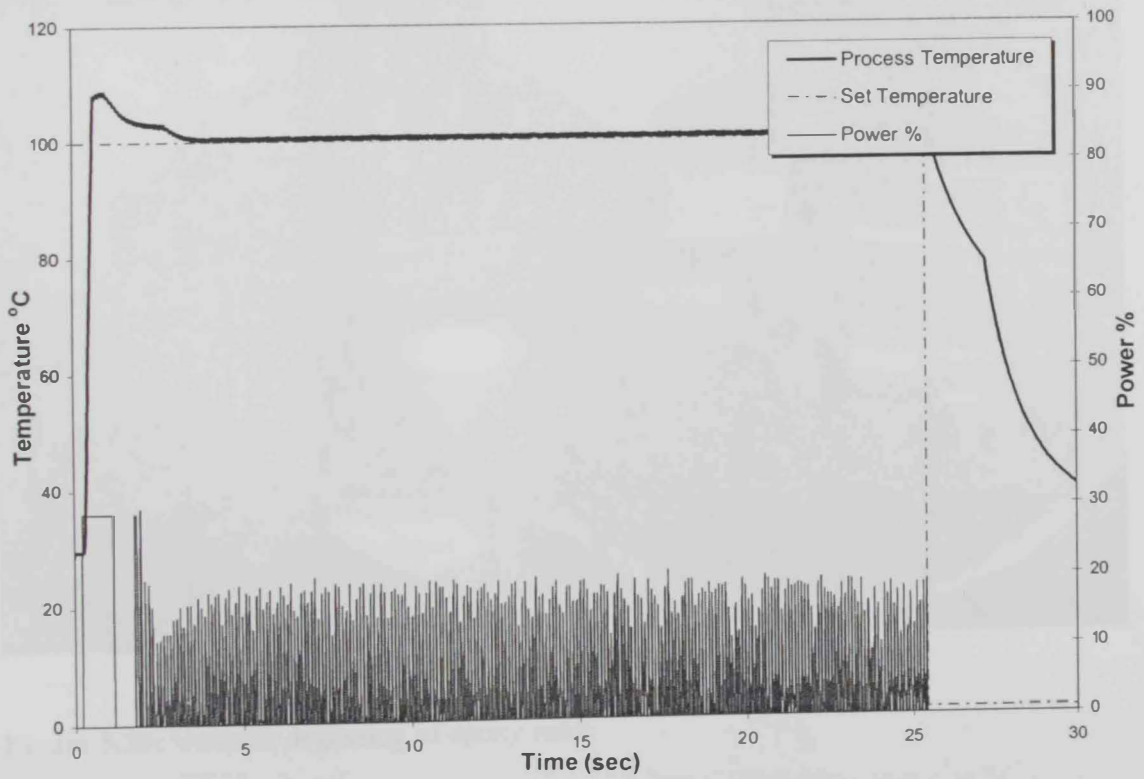

Figure 5.38: Heat Profile of epoxy resin at 200 °C/min for 30% maximum power

5.3.4.4 Effect of Process preparation:

Another issue that largely affects the total cure time is the sample preparation time. This time includes both gel time and vacuum degassing time. Gel time is defined as the time available for mold filling before the epoxy infinite network structure forms. This time was measured to be 45-50 minutes. We have tried to cure the material immediately after mold filling and before gelation and monitor the mechanical behavior. Furthermore, vacuum degassing was applied for additional 50 minutes to reduce the void content [Figure 5.39]. Since the liquid solvent is a relatively efficient dielectric material, the theory we needed to investigate is whether the solvent vapor entrapped and the air bubbles in the resin would affect the properties of the samples. Table 5.9 shows the mechanical properties of the samples cured for 30 minutes with ramp rate at 10°C/min at isothermal temperature of 100°C:

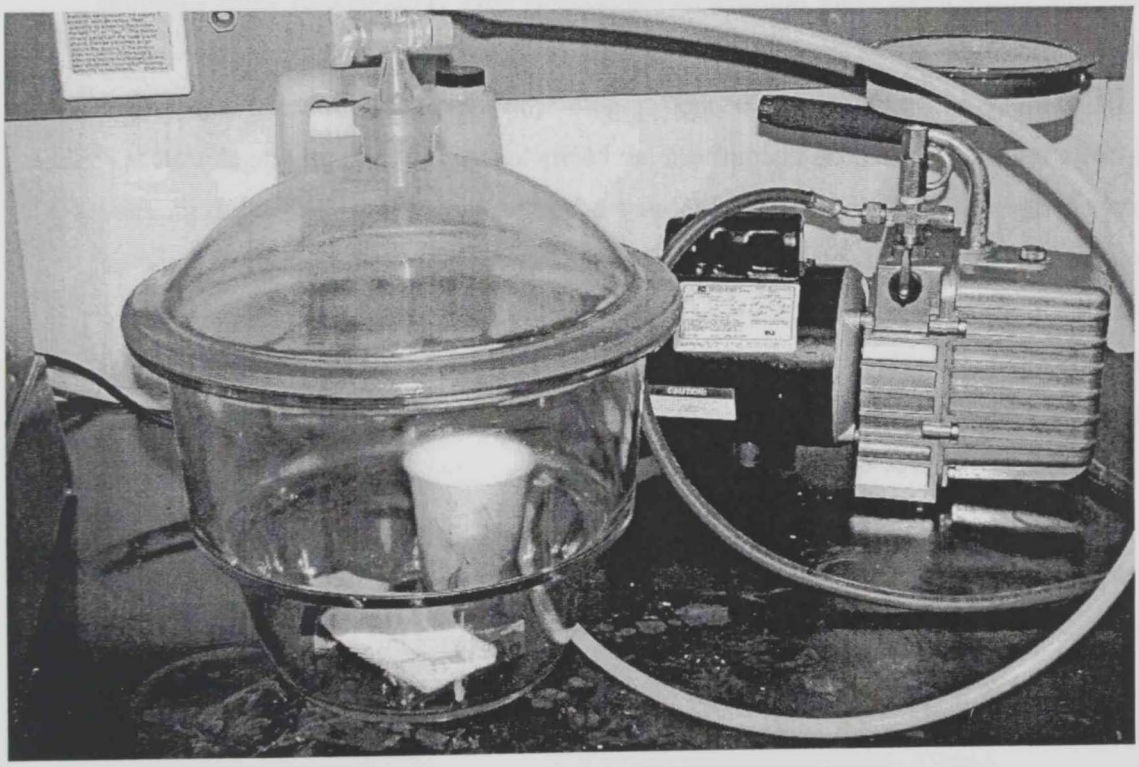

Figure 5.39: Vacuum degassing of epoxy resin

Table 5.9: Effect of Process Preparation on Mechanical Properties of Epoxy Resin cured at 100 °C

Material	Method	Gelation	Vacuum Degassing	Flexural Strength (Mpa)		Flexural Modulus (Gpa)	
				σ_F (S_σ)	A_σ	E_F (S_E)	A_E
Epoxy Resin	Microwave	No	No	71.8 (2.59)	1.96	1.85 (0.22)	0.17
		Yes	No	74.54 (2.21)	1.86	2.71 (0.31)	0.22
		Yes	Yes	75.4 (1.47)	1.02	2.08 (0.37)	0.29

The following remarks can be deduced from the table:

A- Gel time contributed in the increase of the strength from 71.8 to 74.54 and the modulus from 1.85 to 2.71. This is expected as gelation takes extra 45-50 minutes at room temperature. The increase in modulus is more critical. This suggests the importance of gelation to acquire optimum properties.

B- Vacuum degassing has slightly enhanced the mechanical properties. Another effect for vacuum degassing is the decrease in the standard deviation and the average deviation values. In order to avoid time consumption of vacuum degassing a vacuum bag could be used so that instantaneous vacuum is applied during cure. However, the vacuum bag together with the vacuum tubes is required to be made from a microwave "transparent" material so that not to disturb the electric field distribution inside the cavity.

It is worth while mentioning at the end of this section that a calculation difficulty has been faced in the measurement of the mechanical properties. A deviation in sample thickness could lead to error in the mechanical properties values since the depth of the sample is raised to power 2 and power 3 in flexural strength and modulus, respectively. The reason for this difference is the possible leakage of epoxy between the mold mating parts. This phenomenon is especially noticed for Teflon molds as Teflon tends to slightly deflect at high temperatures which lead to minor leakage. For aluminum mold this phenomenon is not significant due to the relative rigidity and dimensional stability at high temperatures.

5.4 Conclusion

In this research we have tackled the fundamental issues in microwave curing of composites. Microwave interaction with materials in addition to the main benefits and challenges of microwave processing were discussed. The literature work in the last 20 years has also been cited and evaluated. Major issues such as homogeneity of the cure, mechanical properties, and cure kinetics were adequately presented. We concluded that the current existing literature can be classified into two categories. The first is a supportive category in favor of the use of microwave energy in materials processing due to the expected higher cure uniformity, higher mechanical properties, and enhanced cure kinetics. On the other hand, the other category has questioned many of those characteristics especially when economic aspects are considered. The highest debate was on whether enhanced cure kinetics and localized superheating are present in microwave energy. However, at least both sides believed in the compatibility of thermal and microwave processing methods when mechanical properties are considered.

Realizing this fact we have tried to prepare a research work that tackles the major areas of debate and challenge. A common remark observed in all the past work is the lack of optimization approach of the problem. The use of power setting, curing temperature, and processing time were randomly selected in most of the time. Therefore, we tried to use more intelligent approach by fixing some process variable such as cure temperature and utilization of efficient process control. Generally speaking, we have based our analysis on two levels: Qualitative & Quantitative.

The qualitative assessment of microwave properties of neat epoxy and fiber reinforced epoxy involved the elimination of thermal runaways and material degradation phenomena experienced in many past research works. Several control strategies were evaluated and eventually a precise control strategy using PID controller has been successfully applied. Successful, defect-free samples were produced at maximum equipment capacity.

The quantitative approach was based on first calibrating the equipment by calculating the efficiency of the heating. This would tell us the actual reliability of the microwave heating and provide an idea on the major heat losses to avoid in future work. An average of 79% efficiency using water samples and 62% using epoxy samples were achieved. Time durations

were also varied based on DSC kinetic analysis to find out the maximum time reduction at the highest possible degree of cure. A fully reliable kinetic model was found to describe the material behavior which will provide a major amount of information for future work as we shall see in the coming section. An extreme heating rate of 200 °C/min were also inspected and found to be possible if the maximum power were carefully adjusted. Gelation time were evaluated and found to be effective in providing high property composites. All the successful samples were mechanically studied by finding the values of flexural strength and modulus. The increase of flexural strength and modulus in the case of microwave curing has agreed with the "optimistic" group. We believe that careful monitoring over process parameters and the homogeneity of microwave curing using feed back controllers is the key reason for this behavior.

5.5 Recommendation and Future Work

From the literature review many research opportunities have been identified as critical building blocks towards optimum use of microwave energy. However, it was not practical to focus on all of them in one research. In fact, the challenge was how to limit these ideas so that to concentrate on a specific, clearly defined approach. For example, microwave effects are a very rich area for research. The issue of cure kinetics enhancement of microwave energy is still a debated area. In our research we assumed similar kinetic behavior for both thermal and microwave curing. This is seen in the use of the DSC data for analysis of microwave processing. The need is to develop a highly calibrated device similar to DSC that insitu measure the degree of cure inside microwave cavity. The microwave generation setup in UAE University can be modified to assure such goal. In fact, a well insulated Teflon molds were designed and manufactured for future research work [Figure A1]. At the same time the controller can be smartly programmed to detect the relative degree of cure or at least the end of cure. By the use of logic blocks and digital signals a small program can be developed to monitor power delivery to a finite amount of epoxy resin during cure. The major issue is to eliminate any source of heat losses in order to obtain a reliability level similar to DSC. This research topic is currently being studied in several universities on both the master and PhD level.

Regarding our area of concentration, the mechanical properties and cure homogeneity, more research can be carried out on carbon fibers. Optimization of this type of fibers is more challenging as the high reflectivity of the conducting fiber represents extra challenge. The primer experimental tests on carbon fibers failed. By careful utilization of the special nature of these fibers the energy reflected can be used to efficiently heat the material. In addition, the increase in sample thickness will definitely complicate the optimization approach. Nevertheless, the microwave cavity can also be modified to include a vacuum bag to reduce void content.

Another issue in optimization of the cure behavior of epoxy matrix is to employ numerical modeling. An objective function can be developed to maximize degree of cure or achieve minimum cure time. The approach is to model the electromagnetic, heat transfer and kinetic behavior of the composites during cure. The three models must be solved simultaneously. Electric field distribution, temperature distribution and degree of cure can then be anticipated at any time step. The energy conservation model can take the following form (Thostenson & Chou, 1999A):

$$\rho_c C_{pc} \frac{\partial T}{\partial t} = k_{xc} \frac{\partial^2 T}{\partial x^2} + k_{yc} \frac{\partial^2 T}{\partial y^2} + k_{zc} \frac{\partial^2 T}{\partial z^2} + \dot{Q}_{gen} + \dot{Q}_{mw} \qquad (5.17)$$

Where ρ, C_p, k, $\dot{Q}_{gen}$, $\dot{Q}_{mw}$ are the density, specific heat, thermal conductivity, volumetric heat generation inside the composite due to exothermic reaction, and internal heat generation due to absorbed microwave energy. The $\dot{Q}_{gen}$ term can be expressed as:

$$\dot{Q}_{gen} = \rho \Delta H_r \frac{d\alpha}{dt} \qquad (5.18)$$

Where ΔH_r is the total heat of enthalpy & $d\alpha/dt$ is the rate of change in degree of cure already defined in equation 5.3. Based on the kinetic discussion in chapter 5 we have already modeled the kinetic behavior of the epoxy resin. Refer to Table 5.1 for more details. In fact, the experimental model found was mainly established to serve future numerical modeling of the process.

Nonetheless, by a method of finite difference time domain (FDTD) programming, which solves Maxwell's equations in time and space, we have already taken serious steps to characterize the electric field distribution in the microwave cavity. The theory of FDTD can be found elsewhere (Huessein, 1995). Our plan was to first provide reliable experimental data and establish an optimization approach. Since the work is still in progress, we decided to put it in the future work section. Yet, some encouraging results have already been achieved. Figure A2 shows a geometrical representation of the waveguide and cavity. The dimensions in the figure are the actual dimensions of the system. Figure A3 visualizes the electric field distribution inside the cavity at the start of the field propagation while Figure A4 shows the field at an intermediate time step. Finally, Figure A5 and Figure A6 show two views of the electric field distribution when steady state has been achieved. In the last figure we can see that the epoxy sample has disturbed the field by absorbing a portion of the wave energy at middle peak. This last figure will be the starting point for any future work in this field. Since Q_{mw} is a function of electric field as explained earlier in equation (2.6), Figure A6 will be the starting point for any future work in this field.

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3- Manufacturing of Parallel Strand Lumber [Online]: http://www.cwc.ca/products/EWP/PSL/manufacture.php

Appendix

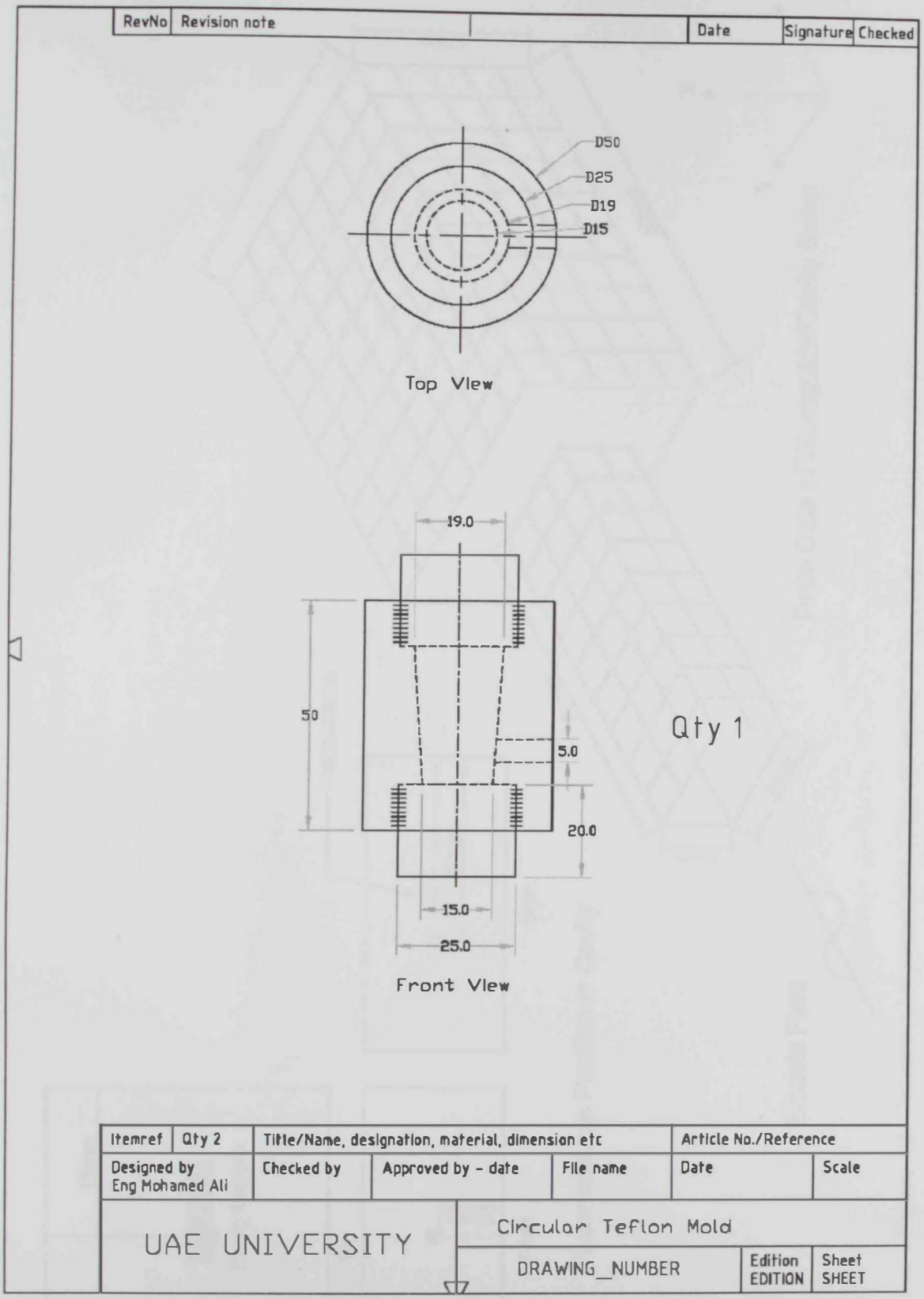

Figure A1: Teflon Mold for study of Microwave Effects

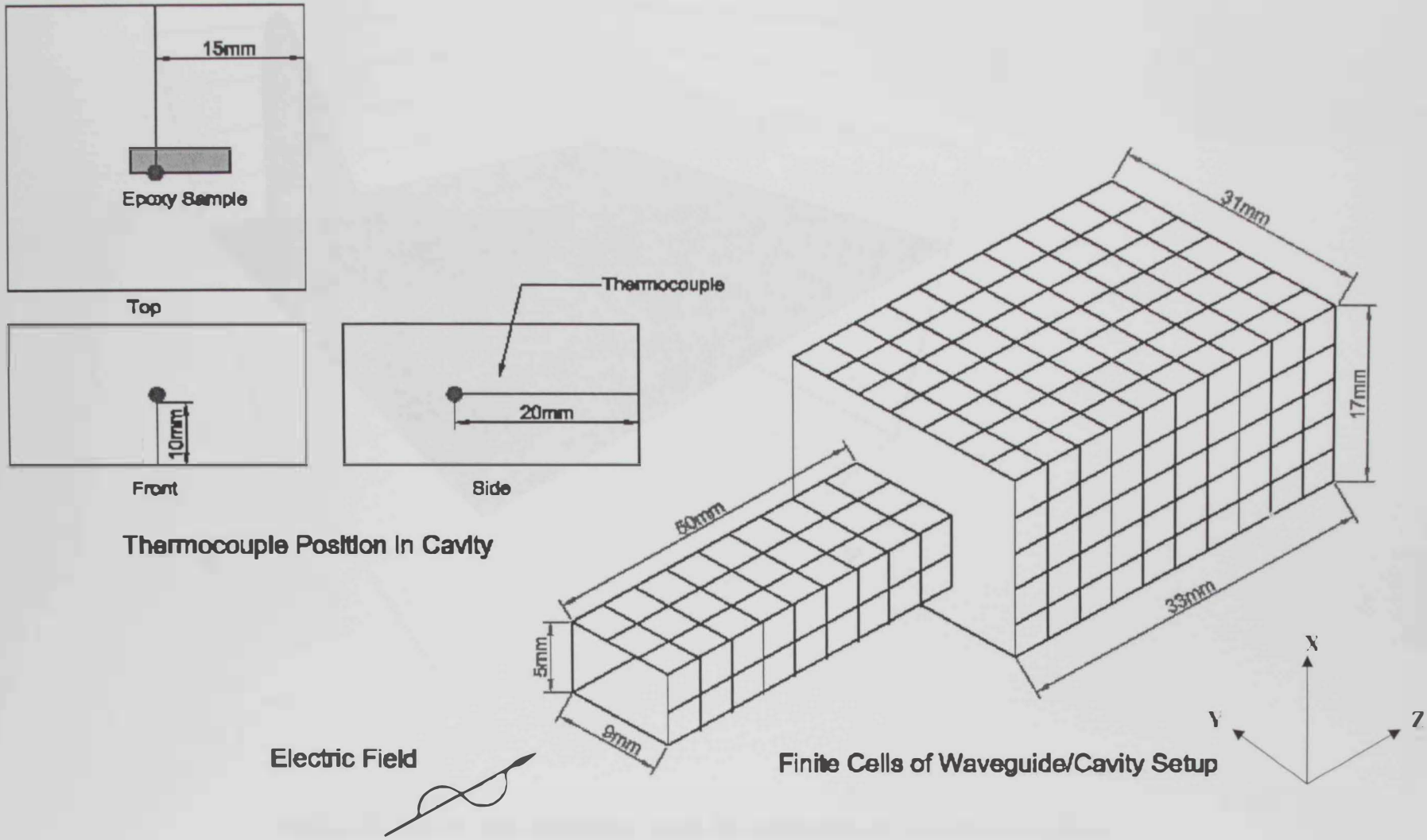

Figure A2: Geometrical representation of the waveguide/cavity setup and thermocouple position in the cavity

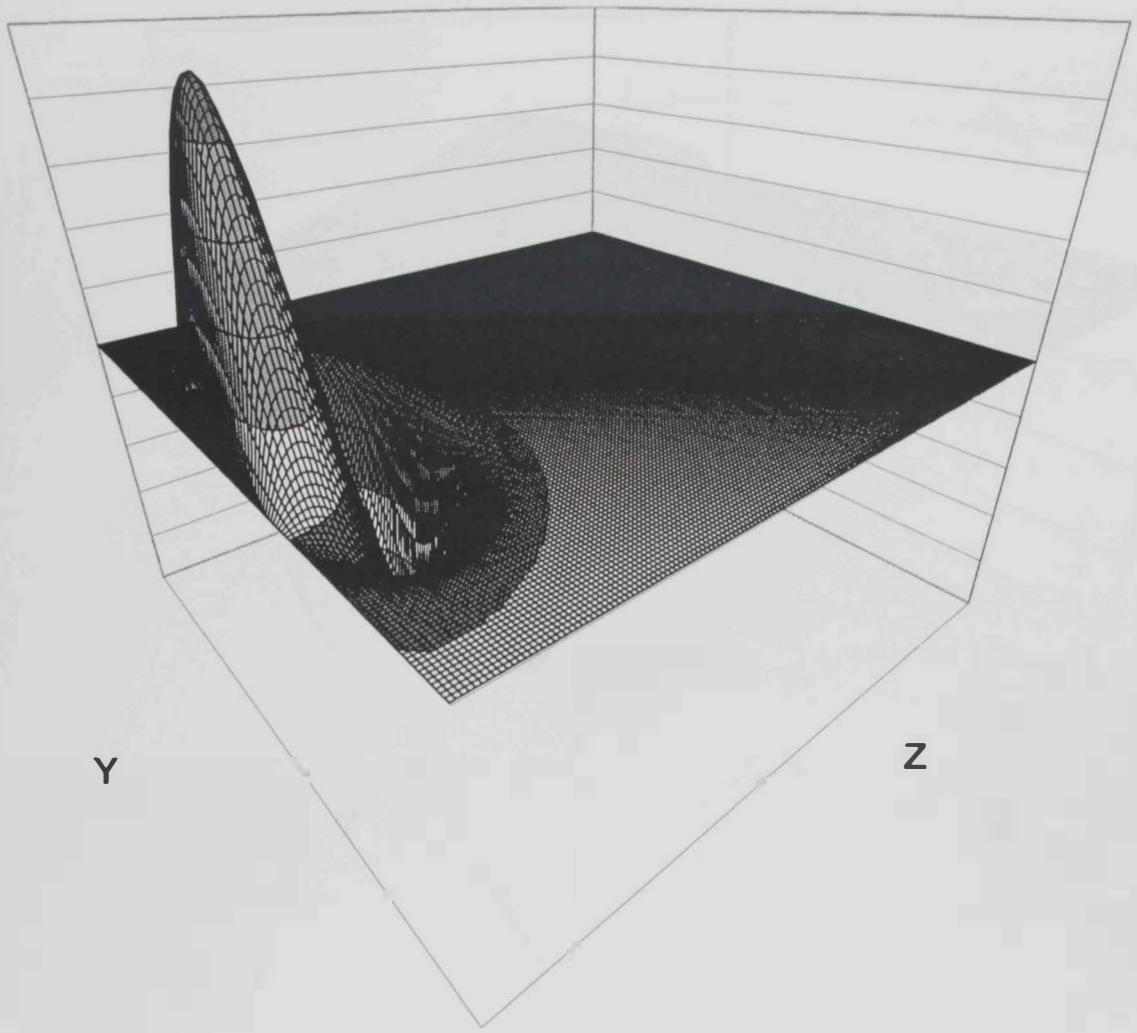

Figure A3: Electric field distribution inside the cavity at the start of field propagation

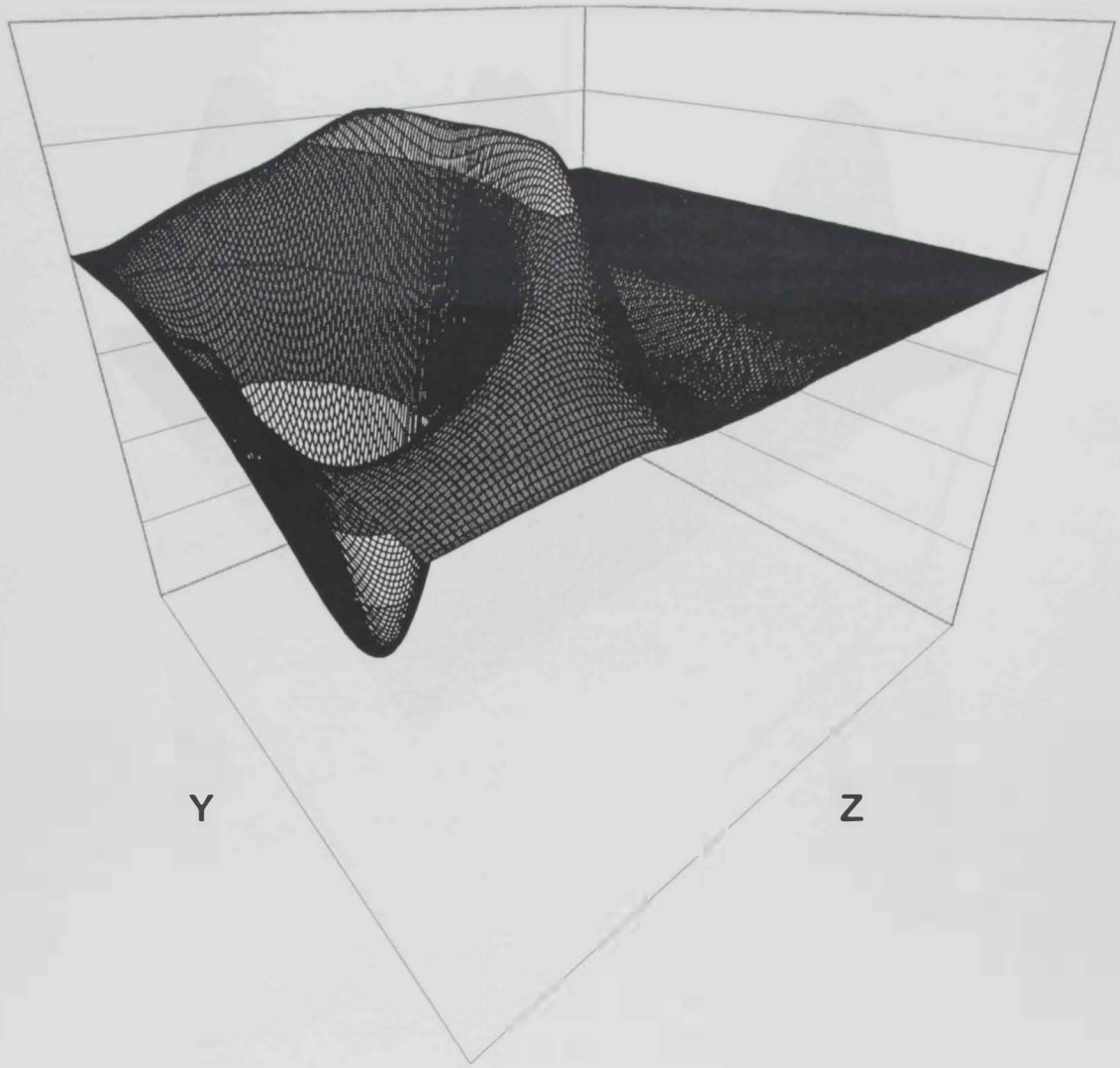

Figure A4: Electric field distribution inside the cavity at intermediate time step

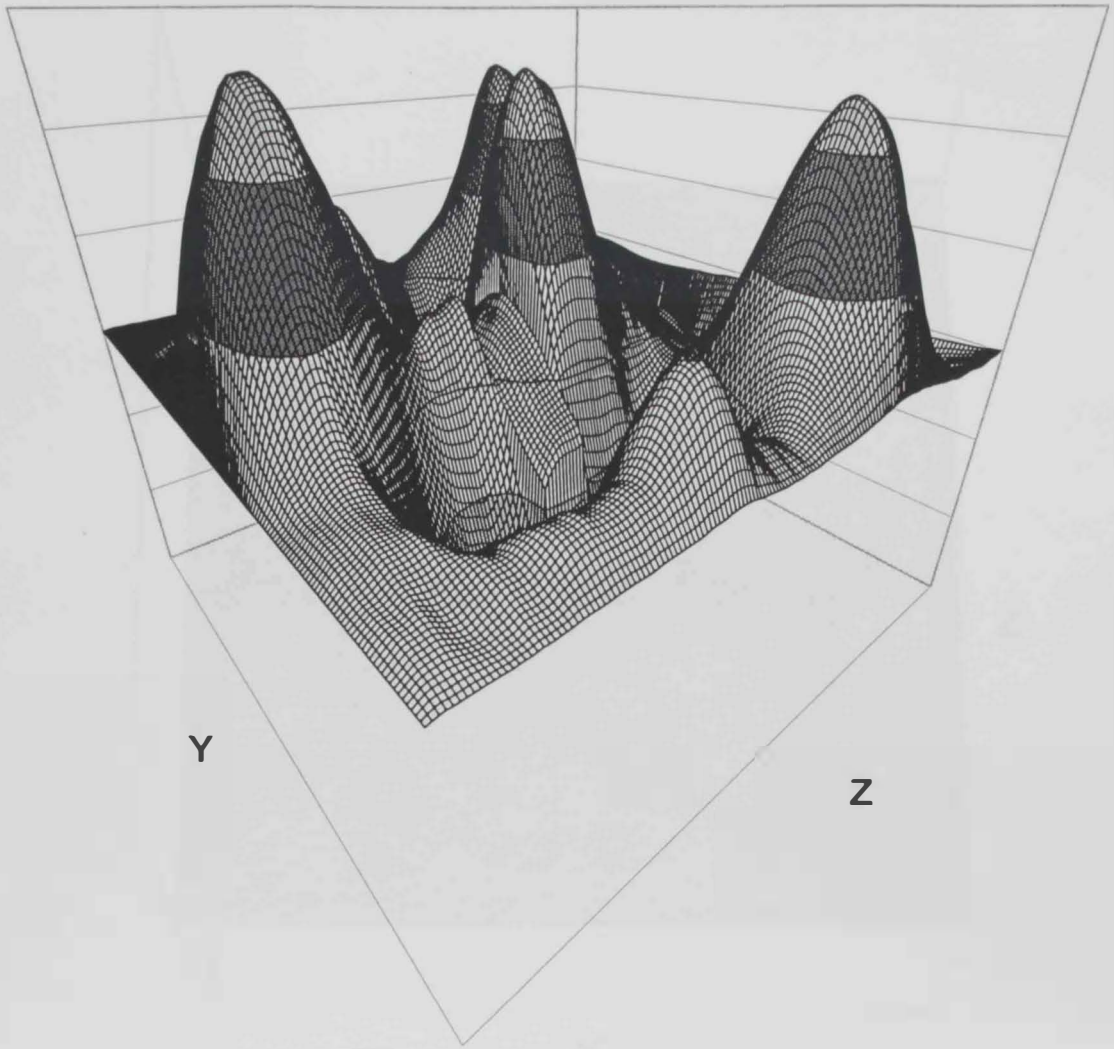

Figure A5 Electric field distribution inside the cavity at steady state

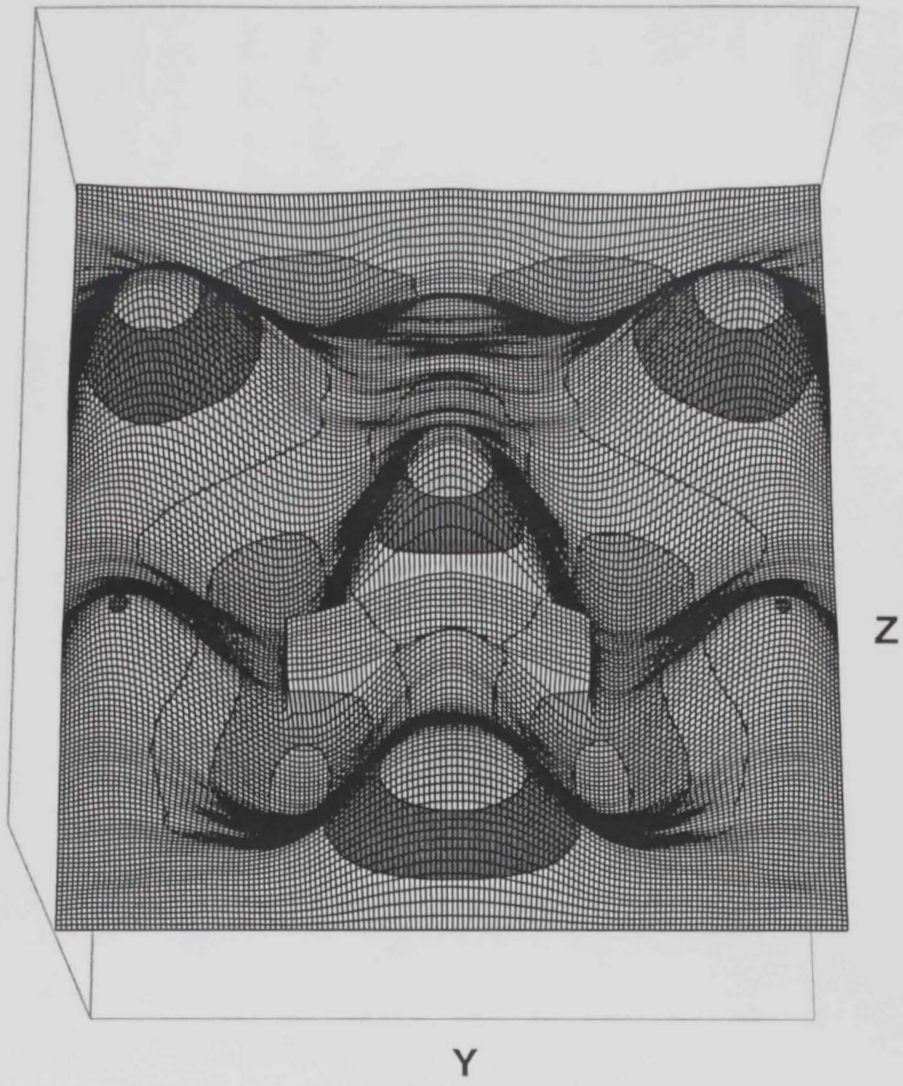

Figure A6: Electric field distribution inside the cavity at steady state (Another View)

معالجة المواد المركبة بإستخدام طاقة الميكروويف

(معايرة عملية المعالجة لمادة الإبوكسي المقوى بالألياف الزجاجية)

مقدمة

لقد أثبتت معالجة البوليمرات باستخدام طاقة الميكروويف أنها وسيلة فعالة لاستبدال وسائل المعالجة التقليدية. هنالك الكثير من التطبيقات الصناعية التي تم تطويرها في كافة المجالات للإستفادة من هذه التكنولوجيا الرائدة خاصة في مجالات الإتصالات والطيران والأغذية وبالأخص المواد المركبة. من أهم أهداف استخدام هذه الطاقة هي تسريع عملية المعالجة والنهوض بالمواصفات الميكانيكية للمواد. لذلك وللإستفادة من هذه الطاقة لا بد من استخدام وسائل تحكم دقيقة للتحكم في مستويات الطاقة أثناء عملية المعالجة. النتائج المرجوة من هذا البحث هو تقليل زمن المعالجة وتوفير وسيلة معالجة متجانسة تمنع حدوث فروقات حرارية كبيرة. لتحقيق هذه الأهداف قمنا باستخدام مولد للموجات الكهرومغناطيسية مزودة بنظام تحكم قياسي ووسائل لقياس استهلاكات الطاقة المنبعثة والمنعكسة من المادة المركبة والتي تتكون من الألياف الزجاجية والإبوكسي. وفي نفس الوقت تمت معالجة المادة المركبة باستخدام الأفران العادية ومن ثم مقارنة المواصفات الميكانيكية مع تغيير زمن المعالجة ومعدل التسخين وأيضا طرق الصب وتحضير المواد الأولية وذلك للوقوف على أفضل وسيلة للوصول الى أعلى قدرة تحمل ميكانيكية.

جامعة الإمارات العربية المتحدة

عمادة الدراسات العليا

برنامج ماجستير علوم وهندسة المواد

معالجة المواد المركبة بإستخدام طاقة الميكروويف

(معايرة عملية المعالجة لمادة الإبوكسي المقوى بالألياف الزجاجية)

رسالة مقدمة من الطالب

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الى جامعة الإمارات العربية المتحدة

استكمالا لمتطلبات الحصول على درجة الماجستير في علوم وهندسة المواد

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